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WITH WHICH IS INCORPORATED THE "CHEMICAL GAZETTE."

A Journal of Practical Chemistry

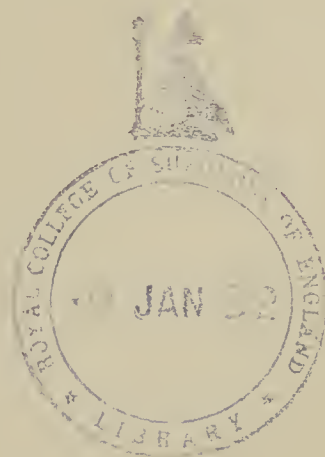IN ALL ITS APPLICATIONS TO

PHARMACY, ARTS, AND MANUFACTURES.

EDITED BY

WILLIAM CROOKES, F.R.S., &c.

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NOTE ON SOME OBJECTIONS TO THE WORK ON SULPHURIC ACID SOLUTIONS.

By SPENCER U. PICKERING, F.R.S.

THE importance of the discussion which took place at the Chemical Society on June 4th (CHEMICAL NEWS, lxiii., 305), on the subject of the hydrate theory of solution, and on my method of examining series of experiments, must be my excuse for answering some of the objections which were raised, and which my already published answer does not adequately meet.

It is scarcely necessary, perhaps, to point out that Prof. Armstrong is quite in error when he interprets the 102 breaks in the figures representing various properties of sulphuric acid solutions as meaning the existence of 102 *different* hydrates, for the same hydrate will account for as many breaks as there were properties examined. The actual number of hydrates of which I found indications in the case in question was only twenty, and I must again protest against the unscientific nature of any objection to their existence on the grounds that their number is greater than we might expect; for we have no right to expect anything at all, being at present entirely in ignorance of the nature or number of those loosely combined and partially dissociated compounds which can exist in the liquid condition.

It is certainly surprising to find Prof. Armstrong producing as a novel discovery, and as the result of his own experience, the conclusion that "changes of composition" (? constitution), "whenever they occurred, were indicated on the curves drawn directly to represent the experimental results"; for this is the very point on which I have insisted all along. Before I had published any of my experimental results, I said (*Nature*, 1889, p. 343), "Differentiation will sometimes bring about the recognition of breaks which might be overlooked in the original curve, for, *though the differential curve can show no breaks which do not exist in the original curve*, it may often, as a consequence of its very nature" (*i. e.*, being more nearly rectilinear than the original curve), "show breaks clearly which would be recognised only with difficulty in the original curve"; while at the commencement of my first paper on Sulphuric Acid (*Chem. Soc. Trans.*, 1890, p. 68) I said, "I would, with the experience I have gained, generally trust as much to the drawing of the original curve as to differentiation, for showing whether that curve is continuous or not, and where the changes occur in it." In my second paper on Sulphuric Acid I used differentiation to a limited extent only, and as affording supplementary evidence to that derived from a study of the experimental curves (*Chem. Soc. Trans.*, 1890, p. 345); while in all the work of this nature which I have done during the last eighteen months I have not used differentiation once (see *B. A. Report*, 1890, 312, and CHEM. NEWS, lxii., 185), although there are undoubtedly some advantages to be obtained through its proper use. Thus Professor Armstrong's experience on this point agrees entirely with my own; so also does Professor Rücker's, though I think that there must be some mistake about his statement that it was a study of my density results which led him to this conclusion, for the original density curve cannot, as a matter of fact, be plotted out at all on any workable scale.

The fact that, in my paper on Sulphuric Acid, I gave a list of the scales which I had found most suitable for plotting out my results seems to have led Prof. Rücker to conclude that the position of the breaks may be made to vary with the scale used. This is certainly not the case (although of course we can select a scale so badly proportioned that it would be utterly useless). I mentioned in my paper (p. 68) that "Drawings on several different scales, and with several different points as origins, were made in all cases, and the labour entailed in the treatment of the results has by far exceeded that of the determinations themselves."

Prof. Rücker's conclusion, that any break which is recognised only in the differential figure deduced from the experimental figure, and not in the experimental figure itself, is "of the most untrustworthy character," is precisely my own conclusion. In the two or three instances in which such indications were obtained I regarded them merely as suggestions (see p. 77 of my paper), and in no single instance did I accept them alone as proving the existence of a hydrate.

Prof. Rücker says that the fact that a series of results may be represented more closely by two curves than by one, may not imply a discontinuity, *because*, by admitting a sufficient number of discontinuities, the results may be represented graphically with absolute fidelity. I certainly fail to see the force of this argument. A drawing which represents experimental results as being entirely free from experimental error is obviously incorrect, and the mere fact that it is physically possible to make an illegitimate drawing of this sort does not throw any discredit on other drawings which are in harmony with the ascertained magnitude of the experimental error. The problem of the correct depiction of results graphically is not a very difficult one; we must adopt the simplest drawing which is consistent with the known experimental error, and discard any drawing which attributes an error to the experiments, either greatly in excess or greatly below that of the observed or probable experimental error. As an instance I may take the diagram which was exhibited at the meeting of the Chemical Society, and which will be found in the July number of the *Phil. Mag.* (xxxii., 94), in my

answer to Mr. Lupton's criticism. It consists of eleven experimental points representing the rate of change of the density with change of composition, and the question is whether these results should be represented by 5 (the greatest possible number), 4, 3, 2, or 1 curves. The safe limit to be assigned to the experimental error is 0·000008 (*Chem. Soc. Trans.*, 1890, p. 71), and depicting these results by—

5	4	3	2	1 curves,

we get—

0	0·000003	0·000008	0·000007	0·000078

as the apparent error of the points. Drawn as 5 or 4 curves, this apparent error would be too far below the experimental error; the 3 curve drawing is legitimate as far as the magnitude of the error is concerned, but, as we can simplify the drawing still further without any increase—indeed with a slight decrease—of the apparent error, we are bound to make this simplification, and to accept the 2 curve drawing in preference to the 3 curve drawing. But no further simplification is possible; for simplifying it one degree further produces a sudden tenfold increase in the apparent error, and makes this ten times greater than the ascertained experimental error. Thus the 2 curve drawing is the simplest, and the only possible representation.

Dr. Morley's objection is, I think, a mistaken one. A break at a particular hydrate by no means implies that this particular hydrate has only just begun to form there. Supposing there to be three hydrates: $CaCl_2$ with 7, 8, and 9 H_2O respectively; then, as water is added to $CaCl_27H_2O$, its effect will be to form some of the $CaCl_28H_2O$, and, as more water is added, the relative proportion of $CaCl_28H_2O$ present will be increased: as soon, however, as more water is added than is necessary to entirely form the $CaCl_28H_2O$, another hydrate, $CaCl_29H_2O$, will begin to make its appearance, and the effect of adding more water now will be to increase the relative proportion of the latter and diminish the relative proportion of the $CaCl_28H_2O$ present: thus the effect of adding water to solutions stronger than $CaCl_28H_2O$ will. will be different to that produced by adding it to solutions weaker than $CaCl_28H_2O$; in other words, there will be a change in the rate of the effect *at* the composition of the $CaCl_28H_2O$ itself: this is just what is actually observed

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AN APPARATUS FOR TESTING THE SENSITIVENESS OF SAFETY-LAMPS.*

By FRANK CLOWES, D.Sc., Lond.,
Professor of Chemistry, University College, Nottingham.

IT is generally acknowledged that the Davy safety-lamp cannot with certainty detect less than 3 per cent of firedamp in the air of the mine. Gas-indicators of much greater sensitiveness have been invented; amongst these the electrical apparatus of Liveing and the spirit safety-lamp of Pieler take first rank. The objection to these special forms is, however, a serious one. They do not serve for illuminating purposes, and therefore it becomes necessary to carry an ordinary safety-lamp together with the testing apparatus. Many attempts have been made to obviate this inconvenience by producing a safety-lamp which shall serve the double purpose of illumination and of detecting minute percentages of firedamp. The discovery of such a lamp would be of great value to the miner, in view of the fact that very low percentages of firedamp have been proved to be dangerous in the presence of coal-dust.

The following apparatus has been devised to render easy the process of testing the sensitiveness of different forms of safety-lamps when used for detecting firedamp.

To enable satisfactory tests to be made in the laboratory, it was necessary to insure (1) the easy and rapid production of mixtures of firedamp and air in known proportions; (2) to insure economy of the artificially prepared methane, which represented firedamp; and (3) to examine the flame of the lamp under conditions as satisfactory as those existing in the mine.

A wooden cubical box of about 100 litres capacity, was constructed so as to be as nearly gas-tight as possible. It was then made absolutely gas-tight by painting it over with melted paraffin wax, which was afterwards caused to penetrate more perfectly by passing an ordinary hot flat-iron over the surface. This testing chamber was furnished with a small inlet tube at the top, and with a similar outlet tube below. It had a plate glass window in front for observing the lamp in the interior, and a flanged opening below for introducing the safety-lamp. This opening was closed by a water-seal consisting of a small zinc tray supported by buttons, and containing about two inches depth of water, into which the flange dipped. A mixer was arranged, which consisted of a light flat board, nearly equal in dimensions to the section of the chamber, and suspended by an axis from the upper corner of the chamber. The mixer was moved rapidly backwards and forwards from the side to the top of the interior of the chamber, by grasping a handle projecting through the front of the chamber.

When a mixture of air with a certain definite percentage of firedamp was required, the methane, prepared and purified by ordinary chemical methods, was introduced into the chamber in the requisite quantity by the top inlet. It displaced an equal volume of air which escaped through the lower outlet, the exit end of which was sealed by being immersed just beneath a water surface. A vigorous use of the mixer secured a uniform mixture of gas and air throughout the interior of the chamber in the course of a few seconds. The lamp was then introduced into the chamber, and placed in position behind the glass window. The simplicity of arrangement of the water-seal rendered the necessary opening of the chamber very brief, and the introduction and removal of the lamp many times in succession was not found to produce any appreciable effect upon the composition of the atmosphere inside the chamber. The appearance and dimensions of the " cap " over the flame were noted as soon as the cap underwent no further change. A lamp was left burning in the chamber for a considerable length of time, and its indications underwent no change owing to the large capacity of the chamber and the very limited amount of air required to support the combustion of the small flame always used in gas-testing. The whole interior of the chamber and mixer were painted dead black, so a to render visible pale and small caps against a black ground.

The methane was introduced from an ordinary gas-holder. A volume of water, equal to that of the methane to be displaced, was poured into the top of the gas-holder. The gas tap of the holder was then momentarily opened so as to produce equilibrium of pressure between the methane and the atmosphere. The gas tap having then been placed in connection with the upper inlet of the chamber, the water tap was opened and the measured volume of water was allowed to flow down and drive the methane into the chamber. As soon as bubbles of air ceased to appear through the water at the outlet, the chamber was closed; the mixer was then vigorously worked for a few seconds, and the mixture of gas and air was ready for the introduction of the lamp. Before introducing the methane for a fresh mixture, the atmosphere of the chamber was replaced by fresh air by removing the water-tray from beneath the opening at the bottom of the chamber, and blowing in a powerful stream of air from a bellows to the top of the chamber.

The chamber was supported on legs, which were arranged so as to place it at a convenient height for

observations through the window, and also for the intro-
duction and removal of the safety-lamp.

The accuracy of this method was tested by introducing
the Pieler lamp into the chamber, which was charged
successively with a series of mixtures containing propor-
tions of methane varying from 0·5 to 4 per cent. The
height and appearance of the cap over the flame abso-
lutely corresponded with a series of standard tests already
published and made by a different method in which fire-
damp was used instead of methane.

The observations were usually made in a darkened
room, but the flame caps were easily seen in a lighted
room, provided direct light falling on the eye or chamber
was avoided.

The capacity of the chamber was 95,220 c.c.; accor-
dingly the following volumes of methane were introduced:
—for ½ per cent mixture 476 c.c., for 1 per cent 952 c.c.,
for 2 per cent 1904 c.c., for 3 per cent 2856 c.c., for 4
per cent 3808 c.c., and for 5 per cent 4760 c.c. It will
be seen that a series of tests, in which the above men-
tioned percentage mixtures were employed, involves an
expenditure of only 15 litres of methane, a quantity far
smaller than that required by any other method of testing
as yet described.

Of many forms of safety-lamp tested in the above
apparatus, the one which most satisfactorily fulfilled the
two purposes of efficient illumination and delicacy in gas
testing was Ashworth's improved Hepplewhite-Gray lamp.
This lamp is of special construction, burns benzoline from
a sponge reservoir, and its flame is surrounded with a
glass cylinder, which is ground rough at the hinder part;
this latter device prevents the numerous reflected images
of the flame, and the generally diffused reflections which
are seen from a smooth glass surface, and which render
the observation of a small pale flame cap very difficult,
if not impossible.

The wick of this lamp, when at a normal height, fur-
nishes a flame of great illuminating power. When
lowered by a fine screw adjustment the flame becomes
blue and non-luminous, and does not interfere therefore
with the easy observation of a pale cap. The following
heights of flame cap were observed, which fully bear out
the unusual sensitiveness of this flame. With 0·5 per
cent of methane 7 m.m.; with 1 per cent 10 m.m.; with
2 per cent 14 m.m.; with 3 per cent 20 m.m.; with 4
per cent 25 m.m.; and with 5 per cent 30 m.m. The
cap, which with the lower proportions was somewhat ill-
defined, became remarkably sharp and definite when 3
per cent and upwards of methane was present. But even
the lowest percentage gave a cap easily seen by an
inexperienced observer.

It appears from the above record of tests that the
problem of producing a lamp which shall serve both for
efficient illuminating and for delicate gas testing purposes
has been solved. The solution is in some measure due
to the substitution of benzoline for oil, since the flame of
an oil flame cannot be altogether deprived of its yellow
luminous tip without serious risk of total extinction, and
this faint luminosity is sufficient to prevent pale caps from
being seen.

From further experiments made in the above testing
chamber with flames produced by alcohol and by hydrogen
it was found to be true in practice, as might be inferred
from theory, that if the flame was pale and practically
non-luminous, the size and definition of the flame cap was
augmented by increasing either the size or the tempera-
ture of the flame. It is quite possible by attending to
these conditions to obtain a flame which, although it is
very sensitive for low percentages of gas, becomes unsuit-
able for the measurement of any proportion of gas
exceeding 3 per cent. This must, for the general purposes
of the miner, be looked upon as a defect; but it is not a
fault of the lamp already referred to. It is of interest to
note that with the Pieler spirit lamp a flame cap an inch
in height was seen in air containing only 0·5 per cent of
methane.

PURIFICATION OF CHEMICALS BY EXPOSURE TO INTENSE COLD.

By H. THOMS.

THE author was informed by Pictet, who has taken out
a patent for the process, that from the purest chloroform
of commerce, if cooled down to about −70°, there
separated out a crystalline body, which is then drained
from the part which remains liquid. This liquid portion
is then exposed to a temperature below −100°, when the
chloroform itself crystallises out, and can be separated
from an impurity which remains liquid.

Chloroform purified in this manner is a colourless
liquid, having at 15° the sp. gr. 1·51. It is in course of
an investigation by O. Liebrich. It is indefinitely per-
manent on exposure to light. Whilst the so-called pure
chloroform of commerce takes a greenish colour if shaken
up with solution of potassium dichromate and sulphuric
acid, if Pictet's chloroform is similarly treated the
chromic mixture retains its yellowish colour. — *Chemiker
Zeitung* and *Pharm. Central-Halle.*

THE BABCOCK METHOD FOR ESTIMATING THE FAT IN MILK.

By FRANK T. SHUTT, M.A., F.I.C., F.C.S.

PAYMENT of money *according to value received* is a sound
principle recognised and acted upon as far as possible in
every branch of commerce. With a view towards its
application in the buying and selling of milk, it is neces-
sary to know at the outset the elements in the composition
of milk that determine the value of the latter for use in
creameries and cheese factories, and, secondly, to apply
some method whereby those valuable elements may be
easily and cheaply determined.

The true commercial value of a milk depends upon its
solid constituents. The variation in the total amount and
composition of these constituents that exists between
samples of genuine milk (due to food, breed, and indivi-
dual characteristics), and the extreme ease with which
water may be added to or cream abstracted from pure milk
without detection by the unaided senses, make it highly
desirable that there should be some rapid and accurate
means, capable of being used by intelligent labour, for
ascertaining within small limits the amount of such
solids. The butter fat is so much the more important
and valuable constituent in the solids that the knowledge
of its percentage in a milk not only protects the buyer
from fraud, but at the same time renders it possible for
the seller to be paid according to the quality as well as
the quantity of his milk—a plan that will commend itself
as an equitable and satisfactory one to both parties.

The Babcock Method.

The usual methods of chemical analysis, while giving
exceedingly accurate results, are lengthy, and must be
conducted by experts in properly equipped laboratories.
Numerous processes, however, have been devised of late
by which the fat may be determined with a greater or less
degree of accuracy in the creamery or factory. Such
processes may be worked by the man in charge, and
require but little time.

Prominent among these methods is the Babcock Test,
which has for its principle the holding in solution of the
solids other than fat by means of sulphuric acid, the fat
at the same time separating as an oily layer. By the
addition of water and the aid of centrifugal motion, the
latter is brought into the graduated neck of the vessel in
which the test is made and its amount at once noted. It
is the object of the present report to bring before the
farmers and dairymen of the Dominion our experience in
the laboratories of the experimental farm regarding the

reliability and accuracy of this process for examining milk.

Examination as to Reliability and Accuracy.

Thirty-two samples of milk have been examined in duplicate by (1) the Babcock test, and (2) by gravimetric analysis, the results by the latter being taken, for the sake of comparison, as correct. These operations gave us 128 independent fat determinations.

As the results obtained throughout the whole series are uniformly close, it will suffice to tabulate here a few of them as examples :—

Milks : "Morning," "Evening," and "Mixed."

No.	Percentage of Fat by Babcock Method.	Percentage of Fat by Gravimetric Analysis.
1	4·4	4·54
	4·4	4·56
2	3·4	3·58
	3·5	3·56
3	3·6	3·72
	3·5	3·76
4	4·8	4·90
	4·8	4·91
5	5·8	6·04
	5·9	6·07
6	3·5	3·40
	3·3	3·35
7	3·4	3·60
	3·5	3·62
8	3·8	3·68
	3·7	3·68
9	3·8	3·87
	3·9	3·88
10	4·0	4·04
	4·0	4·03
11	3·3	3·32
	3·3	3·33
12	3·5	3·70
	3·7	3·69

An inspection of this table will reveal (1) the limits within which the amount of fat will vary when the Babcock test is made in duplicate, and (2) the approximation of such results to those given by carefully conducted chemical analyses.

Of the thirty-two samples tested in duplicate by the Babcock method, only two gave a difference between their duplicates amounting to three-tenths (0·3) of 1 per cent; two varied in their duplicates two-tenths (0·2) of 1 per cent; fourteen differed to the extent of one-tenth (0·1) of 1 per cent; and thirteen gave results identically the same.*

The greatest difference between fat determinations by the Babcock test and gravimetric analysis on the same milk was (0·25) a quarter of 1 per cent. This occurs in three instances only. Where the results are not identical the variation is usually between one-tenth and two-tenths of 1 per cent.

Conclusions.

From these data therefore we may safely conclude that when the Babcock test is made according to the instruction given with the machine, *strictly reliable results are obtained*, and that the percentage of fat so found, allowing for the greatest error possible under such circumstances, will be well within one-quarter of 1 per cent (0·25) of the amount of fat actually contained in the milk.

Recommendations.

Full instructions for operating the Babcock tester accompany each machine. Our own experience, however, leads me here to emphasize one or two particulars, the

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* Since the above was done the Babcock tester has been in constant use for examining the milks produced at the farm. The samples have been tested in duplicate, and the results so obtained show no greater variation than those recorded above.

knowledge of which will assist in obtaining satisfactory results.

1. The milk should be well sampled. If the sample has stood several hours it should be thoroughly, though not violently, shaken before the pipette full is taken out. By this means any cream that has risen is once more uniformly suspended throughout the milk.

2. When a number of tests are to be made the milk of all the samples should be first carefully measured out into the bottles, the acid being added afterwards. When this is completed the two should be *thoroughly* mixed by shaking the bottle in the hand with a rotatory motion. The bottle should then be placed in the machine, which, when all the samples are placed, is immediately set in motion as directed. The thorough mixture of the acid and the milk tends to prevent the formation of curd or scum, which would interfere with the correct reading of the percentage of fat later on. If the bottles are whirled while still hot from the action of the acid, the fat separates more easily and quickly.

3. When the water is added, care should be taken that it is hot. No error can be made by having it too hot.

4. Hot water should also be placed in the machine so that the temperature of the mixture be not allowed to fall.

5. The amount of fat should be noted immediately at the close of the operation, and before the fat has had time to contract through loss of heat.

ON THE AMMONIA-SODA PROCESS.

By H. SCHREIB.

In the year 1876 appeared a report on a proposal of Mr. Thorwald Schmidt respecting the ammonia-soda process. Mr. Schmidt proposes to decompose the liquor of the ammonia-soda process containing chlorides of sodium and calcium, by a solution of the ashes of seaweed. The sulphates of potash, soda, and magnesia contained in the ash of the seaweed are decomposed so far that hydrated sulphate of lime and hydrated magnesia are precipitated in a form which may be available for paper making, as " pearl hardening."

By further adding certain admixtures to the said liquor, at last a pure solution of chloride of sodium is obtained, while, at the same time, iodine, nitrate, and iodides are produced.

The latter solution is then treated again by the ordinary ammonia-soda process for the production of bicarbonate of soda and white alkali. The proposal of Mr. Thorwald Schmidt cannot be generally used, as the ash of seaweed is not to be had everywhere, not to count for the somewhat circumstantial way of proceeding. But the method is based upon a sound idea, viz., the permanent regeneration of the liquor by simultaneously producing useful materials.

I have become induced, by the article of Mr. Schmidt, to introduce to your readers another proceeding practically confirmed for a number of years.

My way of treating the ammonia process is, as far as I know, the only one which has been applied hitherto to practically realise the products out of the said liquor, though I must, however, remark that I have been favoured by special opportunities, and that my idea of treating may scarcely be generally adopted.

A very large German manufactory, making an indispensable article for household consumption, possesses as auxiliary annex a small factory, producing per annum about 1000 tons of ammonia-soda required for the main works. The establishment in question requires, as well, large quantities of cardboard for packing purposes. This latter material, being of a cheap and grey-coloured quality, is also prepared by the same works in quantities of about 10 tons daily.

Owing to its unattractive appearance the cardboard is

to be painted. I had consequently suggested to produce the required " pearl hardening " (*i.e.*, precipitated sulphate of calcium) out of the liquor of the ammonia process, in a way analogous to the one proposed by Mr. Thorwald Schmidt. But this could be done merely by adding sulphuric acid or sulphates.

When decomposing the liquid containing chloride of calcium and chloride of sodium by sulphate of sodium, (Na₂SO₄), the result—

$$Na_2SO_4 + CaCl_2 - 2NaCl + CaSO_4$$
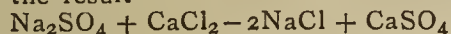
will easily be obtained. The latter one is precipitated in connexion with two molecules of crystal water, and thus forms the wanted " pearl hardening." Besides, there remains a solution of chloride of sodium which may be very well used again for the ordinary ammonia process after it has become somewhat concentrated by boiling. But, however, this course of operating has not been taken by the works in question ; for the manufactory wanted to prepare, if possible, also hydrochloric acid, of which it had need in rather large quantities.

The shortest way to aim at the desired result was to decompose the liquor of the ammonia process by sulphuric acid. The " pearl hardening " was thus precipitated, and an aqueous solution of hydrochloric acid originated therefrom. There is some common salt remaining in the solution too, but this is insignificant, and does not hinder the said proceeding.

The sulphuric acid employed for some years has now become replaced by acid sulphate of sodium, NaHSO₄, owing to the comparatively cheaper price of the latter article.

The weekly production of " pearl hardening," used exclusively for painting the cardboard, amounts to about 30 tons. This way of painting is a highly elaborate one, for it gives to the cardboard a brilliant gloss after it has been salined so far that any lithographic produce may be printed directly upon the cardboard.

Nevertheless, it must be borne in mind that every manufactory will not be able to make the above-described advantageous use of the liquor out of the ammonia process.

A similar proceeding may, notwithstanding, be adopted in general, provided the works will be able to combine the production of hydrochloric acid with the preparation of sulphate, viz., the first part of the soda manufacturing according to Le Blanc's method with the ammonia process. The hydrochloric acid would then be saleable as usual, whilst the sulphate of sodium would be left for the decomposition of the liquor containing chlorides of sodium and calcium out of the ordinary ammonia process. Pearl hardening would be precipitated, and a solution of pure chloride of sodium originated. This solution, as soon as properly concentrated by boiling, may be again treated in the ordinary way for the production of bicarbonate of soda and white alkali.

At any rate this proceeding it to be highly recommended, for it possesses the great advantage that all materials may be conserved or reproduced. There is no loss of material whatever but the trifling though inevitable one caused by the manufacturing itself.

Chlorine is obtained in the form of hydrochloric acid, except the small permanently circulating quantity. All the sodium is converted into soda, and the pearl hardening contains sulphuric acid as well as calcium. The production of hydrochloric acid through the proposed way of operating is very well worth mentioning, as the ordinary ammonia process does not admit that result.

The new proceeding can be adopted in all those places where there is a good market for pearl hardening, which I have no doubt will be the case everywhere in Western Europe. Pearl hardening is a well-esteemed stuff for a great many sorts of paper. It is furthermore very available for the painting of cardboard as shown above. The box-makers using cardboard painted by means of pearl hardening will save any expenses for labels, &c., as all printing matters may be lithographically printed directly

upon the painted cardboard, and, by the modern box-making machineries, cardboard thus prepared can easily be shaped to boxes of any sort and size that will be required.

As shown by the aforesaid facts, the manufacturing of soda according to the ammonia process, even on a small scale pays very well. The profitable realisation of the returns must be taken into consideration to be sure, but, even without that good chance, the making of soda turns out most advantageously, in particular for large concerns carrying on the same in an auxiliary way in order to produce the soda required for the main works.

Owing to the Soda Rings driving up the prices for the article, it is worth while to keep this point in view.

As far as I know, some important German makers—being large consumers of soda—are about to prepare their own ammoniated soda, in order to become independent of the fluctuations of the market.

CONTRIBUTIONS TO MICRO-CHEMICAL ANALYSIS.*

By H. BEHRENS.

(Continued from p. 304).

FOR evaporations with hydrofluoric acid, as also for ignition and fusion, the author uses platinum spoons of 9—15 m.m. in diameter, and for igniting or melting small specimens platinum wires, as for blowpipe work. The greatest care must be taken in cleaning these spoons and wires. The spoons should be of the short-handled pattern, made in one piece, without rivetting.

Bunsen burners with a double gas supply, which give a small luminous flame if the regulating tap is closed, are very suitable for micro-chemical work if the luminous flame is small enough. It must not be higher than 10 m.m. It is difficult to make the flame of a spirit lamp small enough. Fatty oils answer the purpose well if a single thick thread of cotton is used as a wick.

The ordinary dropping tubes yield drops of about 0·05 c.c. ; these are much too large for micro-chemical work. If the utmost nicety is required, drops of 1 m.grm. may be used, which spread out on the glass to discs of 2 m.m. in diameter. The limits for the sensitiveness of reactions, as laid down below, refer to such milligramme drops.

In order to manipulate such small quantities of liquid we use capillary tubes, obtained by drawing out thin bent tubes. They have the advantage, as compared with slender pipettes, that they can be expeditiously prepared, which enables us to dispense with tedious and uncertain cleansing. For distilled water a pipette may be recommended with a point so fine that, if applied for a moment to the port-object, it gives drops of 2—3 m.grms.

For manipulating the reagents, may be used platinum wires of 0·5 m.m. in thickness, melted into glass rods, or glass threads of the same thickness. The hooks of a finer platinum wire, formerly recommended, have the advantage, when they are thoroughly cleaned, that they always take up approximately the same quantities of liquids. Their defect is that a perfect cleaning is not as easy as with a straight stout wire, which can be made perfectly clean in a few seconds by wiping, rinsing, and ignition.

Reagents.

A catalogue of reagents may be found in the *Annales de l'Ecoles Polyt. de Delft*, 1891. It may here suffice to remark that some of them, *e.g.*, the salts of cæsium and thallium, are not used in the ordinary course of analysis. The manner of their application is peculiar, since they are used in saturated solutions, or even as powders. The reason of this is that we must work with the smallest possible volumes of liquid. Reagents in powder have also the advantage that they come into action more slowly

and simultaneously in all degrees of dilution. Most reagents are used in such small quantities that a stock for more than a year's service may be kept in specimen tubes of the smallest sort. Hydrofluoric acid and ammonium fluoride may be conveniently kept in similar tubes of ebonite, in the caoutchouc stoppers of which thin platinum wires may be conveniently fixed, coiled up at their free end into a loop or a spiral,

The selection of reagents, even if arranged for all contingencies, takes up little room.

Operations.

The evaporation of dilute solutions is generally effected on the object glass. If high concentration is necessary, the solution is let fall, drop by drop, upon the heated spot of the glass, by means of a small pipette. A current of dry air expedites evaporation and prevents boiling. When the last drop is about half evaporated the object slip is quickly cooled. The partial evaporation of single drops is often requisite, and occasions much trouble to beginners. A thin glass and a small flame are the most essential conditions. The object slip must almost touch the point of the flame, and the refrigeration must be effected as quickly as possible. By means of the following simple expedient it is possible to evaporate the smallest drops over a free flame without the danger of their entirely drying up. Upon an object slip, and near one end, there is laid a covering-glass ; the drop to be heated is placed upon this, and heated as usual over a small flame. When the proper degree of evaporation has been reached, the covering-glass with the remainder of the drop is made to slide upon the cold half of the port-object. Evaporation by heating the port-object always invariably occasions the formation of irregular crystals on the edge of the drops, and this evil is the more perceptible the further the heating extends over the glass. Evaporation at the ordinary temperature (*e.g.*, in an exsiccator) generally produces uniform crystallisation ; the same is the case if the glass is cooled and the drop is heated by blowing warm air upon it from the nozzle of a blowpipe strongly heated.

For sublimations the specimen is placed near one of the corners of the port-object and covered, after it has been moderately heated, with a shorter slip with its corners bent downwards. For sublimation at a red-heat, and for subliming fluorides, we use small platinum spoons covered with platinum foil or covering-glass. The necessary cooling is effected in this case by the application of a drop of water. For filtration there are substituted, as far as possible, decantation and absorption with filter-paper. It often occurs that a drop of liquid must be separated from crystalline or powdery sediment without the necessity for complete clarification. This can generally be effected as follows :—A clear portion at the margin of the drop is drawn out into a streak of 1 c.m. in length, and its end is gradually widened to form a drop. The speed at which the liquid streams over depends on the inclination of the port-object and on the expansion of the thread of liquid. The rest of the liquid is drawn away through the connective channel by means of a platinum wire held in a slanting position, and intercepted with a small roll of filter-paper. The washing is effected in a similar manner, small rolls of filter-paper serving to suck up the rest of the washing water. If complete clarification is needed, or in case of light flocculent precipitates, such as basic iron or aluminium acetates, the iquid may be allowed to subside in a tube pipette of 2 m.m. internal diameter, the upper end being closed with a wax plug. The deposition may be hastened by the addition of washed barium sulphate during precipitation. and by centrifugal action. If the liquid is sufficiently clarified allow it to flow, drop by drop, upon burnt clay or compressed filter-paper. Here it forms little lumps which can be washed with a couple of drops of water, and scraped off with a slip of sheet platinum.

(To be continued).

THE PROGRESS OF CHEMICAL THEORY: ITS HELPS AND HINDRANCES.[*]

By Dr. PERSIFOR FRAZER, Prof. of Chemistry.

IT is the ordinary reproach to science of the ignorant and disingenuous, that its conclusions at any given period are no more stable than the wildest speculations of the fanatic and dreamer.

We read continually in the papers some arrant nonsense said to have been pronounced by " one of the eminent scientists " of such-and-such a place and time, which the course of events has disproved ; and the public is left to the conclusion that the gains of science are only air castles certain to dissolve when they become unpopular, and certain to lose popularity when the first pleasurable effect of the announcement has passed away. The following extract, from the *St. Louis Republic,* will furnish a case in point :—

" It has only been sixty years since a great mathematician demonstrated that a steamship could never cross the Atlantic because it would be impossible for her to carry enough fuel to last during the trip. Before he had hardly deduced his calculations a steamer from America glided into port."[†]

The name of the eminent scientist is not mentioned, and it is safe to conclude that if any man made such an observation he either would have failed of recognition by the class to which he is said to have belonged, or he was false to the fundamental principles of inductive science. It is not the province of inductive science to establish what is impossible, but what is in various degrees likely. Its premises are facts and its conclusions are probabilities ; in many cases weak, but in others so strong that they produce the same effect upon the mind as certainties. Nor is it true that the gains of science are evanescent. Parallel with the accumulation of observations run the generalisations upon them. These generalisations are usually passed through the purgatory of hypothesis before they attain the bliss of theory, but no theory is old enough yet to have become more than a theory, though some have stood so many tests of their truth as to carry the conviction of axioms.

In looking over the histories of the sciences one finds the same general course of progress. At the outset in the halcyon days of the old Greeks, it is likely that some wise words will be found to have been spoken concerning them all ; words that astound us with the apparent insight they show into problems which it would seem that the last twenty-five centuries were needed to give. But the centuries were not all equally productive. There came across the path of every systematic study of the laws of nature, first the cultured blight of the Aristotelian philosophy, which assuming to know everything, in fact largely contented itself with verbal jugglery, whereas accumulation of facts was the only road to knowledge ; obliterating the forward steps that had been made, and substituting in their place the evolution of the universe and its laws from within. It was a philosophy where the distinction between words and things was obscured, and

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[*] Introduction to the Chemical Lecture Course at the Franklin Institute, November 10, 1890.

[†] In reference to the supposed steam engine prediction, Mr. W. P. Tatham calls my attention to the fact that the actual observation misquoted by the *New York Herald* for sensational or other satisfactory journalistic reasons, and repeated ever since (in spite of countless corrections), after the manner of the average erroneous newspaper paragraphs, was made by Dr. Dionysius Lardner and referred to the steamer of that epoch, which, according to his calculation, could only carry coals for a journey of 2000 miles, with due allowance for accident and delay. That he never entertained such an opinion as that above referred to is evident from the following language : " We are even now upon the brink of such improvements as will probably so extend the powers of the steam engine as to render it available as the means of connecting the most distant parts of the earth."

" The Steam Engine Familiarly Explained and Illustrated, &c.," by the Rev. Dionysius Lardner, LL.D., F.R.S., pp. 241—242, &c., &c. E. L. Carey and A. Hart, Philadelphia, 1841.

a natural fact was attained by means of a pretty syllogism.*

Vastly worse were the centuries which followed, known as the middle ages. Centuries of ignorance, selfishness, and crime; when the possession of any knowledge but that of an armourer was looked upon with distrust and ascribed to the devil.

The different natural sciences emerged from this barbaric condition one to three centuries ago, and under the liberty of enlightenment, with the stimulus of more general education, have attained an abode in the life of the race from which it is difficult to see how they can be displaced without such a general cataclysm as would nearly destroy the human race itself.

Amongst these sciences, that of chemistry has had such a marvellous career that it is, perhaps, the best example which could be selected of the progress just alluded to. It illustrates aptly not only the methods employed in building up an inductive science, but the things that have helped and those that have hindered a development which, nevertheless, in spite of all hindrances, must fill us with a sense of wonder.

Our reason for this is that from various causes the real growth of chemistry only began in the seventeenth century, and that even then it lost nearly a hundred years in the quagmires of a false hypothesis which not only directed the efforts of chemists into unfruitful fields, but destroyed the value of the conclusions they reached from their work. Yet, even with all these drawbacks, no domain of human investigation has been widened so rapidly and with such advantage to the world.

At the very outset of the subject we find a generalisation of old Democritus (who lived 450 B.C.) so astounding in its character and so accurate in most of its statements that only in the past few years have chemists been able to reach these profound thoughts thrown across the ages into the midst of the civilisation of our time, as the legend has it that Bruce's heart was thrown by the Douglas into the hosts of the Saracens to stimulate the ardour of the Christian Knights to charge and recover it. But, unfortunately, no such effect was produced by the good old laughing philosopher; though at a snail's pace, and after a lapse of 2300 years, we have reached the spot. Briefly, as transmitted to Epicurus, and expanded by Lucretius B.C. 99—55, it was this.†

The universe consists of atoms and space. The atoms are of many forms and of different weights, and the number of atoms of each form infinite. Change is only the combination and separation of atoms ! Atoms are in constant motion. "First beginnings" or atoms are never destroyed or worn out. The difference between a hard body like iron, and a soft body like air, is that in the first the atoms move to and fro within small distances; in the soft body they move freely or rebound from each other only at long intervals.

Bodies are partly "first beginnings," partly unions of "first beginnings." The properties of the bodies formed of the groupings of "first beginnings" need not be like the properties of the "first beginnings" themselves. "It matters much with what others and in what positions the first beginnings of things are held in union and what motions they do mutually impart and receive."

These views are extraordinary, and, with the exception of the difference in the form of atoms, which is a point beyond what we have been able to reach even now, the above contains a very fair statement of the atomic theory which is held by the most advanced chemists to-day.

How Democritus could have reached such conclusions is a mystery, but his annunciation of these recondite truths very well illustrates the fact that an hypothesis, be it never so beautiful and even true, if unaccompanied by

facts to support it in no way helps the progress of natural science. Like every other guess it indicates merely the frame of mind of the man making it. It is like a floating shadow on the sea of time. Perhaps it defines substance, perhaps only a cloud of fancy.

This seed thrown off by Democritus found no soil of facts on which to grow, from his time until late in the present century, although Gassendi, Canon, and Provost at Digue, in France, after ages of ignorance, proposed it again, but without proof; and it is thought to have influenced the minds of Newton and Boyle.

This then is one example of an occurrence in the history of the science which to all appearance neither helped nor obstructed its progress unless in the indirect way of teaching men's minds to grasp large and comprehensive thoughts. All could not have been ignorance and degration in Abdera (Thrace), or Miletus, or Athens, where a language existed capable of conveying from mind to mind thoughts like these, and where a mind was capable of conceiving such thoughts.

It teaches the student of natural history a lesson in addition to that of the old traveller's speculations, and it may serve to illustrate the difference which the late Prof. Clifford of Cambridge pointed out between accepting those conclusions of natural science which one has been taught, but has not personally investigated, and accepting what is said to have been revealed, but which, it is acknowledged, is not susceptible of any proof. In the one case the way is open to any one to pursue any single direction which has been before taken; measuring and judging of the correctness of the steps of one's predecessor; but in the other case there is no path anywhere, and the correctness of the position assumed cannot be judged. It is the difference between, on the one hand, handing the keys of a hundred trunks to a custom house inspector, who has at best time to examine but one or two, asking him to satisfy himself of the accuracy of your description; and, on the other, telling him that something indescribable ought to convince him more thoroughly of the contents of the trunks which he cannot inspect than of those which he can. Speaking generally it may be said that a proposition of which the steps which led to its acceptance cannot be indicated and followed has no place at all in the domain of science, though it may be true.

Such propositions were those of Democritus above given, and it is quite just that in the absence of logical proof they should have been excluded from the realm of science, and that to him who first showed reason for believing them should be accorded the honour of their discovery.

Of much less importance is the next hypothesis of the nature of things which we find annunciated by Aristotle in his quadrilateral of states: solid, fluid, dry (or warm), and moist (or cold), or what he supposed to be the elements of all bodies, viz., earth, air, fire, and water. It was unfortunate, and yet in accordance with the usual march of events, that this utterly inadequate and narrow guess should have fettered men's minds for 2000 years, owing to the mighty hold which Aristotle took of all nations. (See Aristotle, " A Chapter from the History of Science," Lewes).

As his historian remarks, Aristotle's works had a prodigious influence in Asia, and Europe, and Africa; among the Persians, Arabs, and in Germany, where part of his ethics were read in the churches on Sundays instead of the Bible. In the middle ages, too, these elements of Aristotle were imbued with a mysticism more than Platonian.

It was the spirit of that middle age, when the ignorant classes being the powers, made patient scientific work difficult and dangerous, that learning was concealed under the mask of paradox and cryptogram as if it were a crime. Whatever Aristotle's view of his elements may have been, it took a new direction, beginning with Geber in the eighth century

The first chemists were alchemists who sought the

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* It is intended to refer here to the exposition of the Aristotelian philosophy by its disciples from about the time of the Christian era to the eighteenth century, and not to disparage the marvellous genius of Aristotle.

† *Democrit-Aderitæ operum fragmenta.*

transmutation of base metals into gold ; the philosopher's stone, and the elixir of life. These were represented by Geber (an Arabian alchemist of 760), Albert von Ballstädt (1193—1280), Roger Bacon (1214—1294), Raymond Lull (1235—1315), Arnald de Villanova, Caletonia (1235—1314), &c. Those who examined physical problems retained the Aristotelian view, while the alchemists took more or less modified forms of Geber's doctrine, that the metals were composed of mercury and sulphur. As an instance of the confusion which reigned in the ideas of this time, some believed that these constituents of metals were real sulphur and real mercury, while others believed that qualities were intended by these terms. Geber ascribed to the sulphur the property of giving different colours to the metals.

At the end of the fifteenth century the alchemists had added salt to mercury and sulphur. Many regarded the Aristotelian elements as the ultimate ; and mercury, sulphur, and salt as the intermediate or proximate elements, as, for example, Basil Valentine, who extended the number of substances of which these were the ultimate elements, from metals to all known matter, but denied that they were the common substances which we know under their names.

In the early part of the sixteenth century the failure to find the philosopher's stone led to the decadence of alchemistical or transmutation chemistry, and the rise of iatrochemistry or that of healing. Paracelsus (1493—1541) taught that in a burning body the sulphur quality represented the inflammability, the mercury the sublimation, and the salt the ashes.

From this to the end of the seventeenth century disputes as to tenets were numerous, but no real progress was made, Agricola (1490—1555) attacked Paracelsus and fell back upon Aristotle. Libavius wrote the first treatise on chemistry (1595). Van Helmont (1577—1644) denied all Paracelsus' views and sought an universal solvent, which should be a panacea. He first recognised the existence of gases and quantitative relations, and opposed Aristotle's doctrines that fire was a body or earth an element ; but believed water and air were such.

Glauber (1603—1668), though possessing variable views, invented better means for separating bodies. Sumert (1572—1637), Willis (1621—1675), Lemery (1645—1715) believed in five first principles—mercury (spirit), sulphur (oil), salt, water (phlegma), and earth. Lemery taught that these were in rapid motion, and thus gave rise to the obvious properties of things. He explained the well-known phenomenon of the calxes of the metals weighing more than the metals themselves, by supposing that in burning they absorbed fire materials.

The real philosophy of chemistry commences with Robert Boyle (1622—1691), who denied the accuracy of the doctrines both of Aristotle, and the later alchemical and iatro-improvements upon them. He believed that heat had not the power to transform complex substances into their constituents, but, on the contrary, sometimes produced complex out of simple substances, and sometimes was without effect. Other agencies than heat could produce the same effects. He strongly denied that one could predict the number of simple substances as Aristotle and his successors had done. He thought it probable, however, *that the so-called elements consisted of the same kind of matter*, differing only in the size, form, &c., of their respective smallest parts (see Kopp's *Geschichte der Chemie*).

It is well to pause for a moment here to consider these logical and scientific views of Boyle, not alone because they introduced for the first time a rational inductive system of chemistry, emanipated from the mysticism and superstition of the ancients, but also because they are typical of one of the greatest of helps to the progress of chemical theory, independent and fearless criticism.

Except the brilliant guess that the so-called elements consisted of the same kind of matter, Boyle's mission seems to have been to hew down the weeds and under-growth which had impeded the march of the science ; yet his services were invaluable, as without them no further progress could have been made. This fact illustrates also the injustice of the cry so popular in some cases when the fallacy of a proposition has been exposed :—

" What have you to set up in its place ?"

Surely it cannot be required of him who discovers a flaw in a supposed explanation that he should be always ready with a sound explanation. The two characters of mind which are required to accomplish these very different tasks are entirely unlike.

Plato and Aristotle probably regarded the lightning stroke as a natural phenomenon, and could have refuted the popular belief that it was the missile from Zeus's hand, but it required dozens of centuries of observation before even the most remote approach to an explanation of the phenomenon could be given.

As soon as the ground is cleared of rubbish, other and more rational theories have a chance to grow. Therefore the iconoclast, if impelled by his sense of truth, and if considerate in his methods, is a necessary pioneer and axeman ahead of the great army of Science. It is so much easier, however, to throw down than to build up, that the iconoclast business is often overdone by those who are incapable of any more skilled service to Science, and who confound the art of attacking everything with the duty of overthrowing evil. All honour to Robert Boyle for calling a halt in the unbridled fancy of the chemists of his day, and clearing the way for a new era ! All honour to his deep insight into the workings of Nature, that he announced independently what old Democritus had dimly foreshadowed 2000 years before ; and what it was reserved for a great chemist now living to put in words and carry almost to the state of an accepted theory : yet to neither of them will belong the credit of demonstrating the unity of matter, but to some one, it would seem, who shall pass the speculative stage and offer proof. It looks as if this were not to be long delayed.

Both by Boyle's destructions and by his conceptions he aided the progress of chemical theory, as few have done since his time ; and chemistry, or the study of the most intimate relations of matter, as distinguished from alchemy, magic, or the healing art, may fairly be said to have started with Robert Boyle.

Singularly enough the first sapling to spring up and occupy the new clearing made by Boyle was an error so gross that it seems to the youngest student of to-day grotesque in its clumsiness, and yet, defended by some of the subtlest of sophists, it took 100 years to overthrow it. And the most instructive part of its history is that it was finally overthrown by an argument which Boyle himself had employed, — which had been employed by other sceptics, and explained away by the phlogistonists, and was ultimately and successfully refuted with the same experimental proof by a countryman of Boyle. It is often the case that an attack in front, over the very ground of numberless previous repulses, is successful, and it was the case here, as shall be briefly shown.

Stahl (1660—1734) was a physician of independent views, who adopted Becher's theory of combustion or the changeability of bodies by heat. He believed that he had settled experimentally this question : — " Is a common quality present in sulphur and carbon ? or is one contained in the other ?

The generally accepted view at that time was diametrically opposite to that which Boyle held of combustion, and might be stated thus :—Sulphur consists of oil of vitriol and some combustible body, which latter escapes in burning. Stahl combined oil of vitriol with an alkali, and, heating the combination with carbon, obtained an alkaline sulphide similar to that produced by sulphur and an alkali. From this, sulphur (or vitriol) can be separated.

Therefore, the combustible in carbon and sulphur was the same !

Heating calxes of the metals with carbon, there resulted the metals. The metals were then composed of the calxes and this substance. Fats and oils produced the same effect with the calxes, and, hence, in them too was the same combustible substance.

Stahl called this combustible "Phlogiston."

This hypothesis was rapidly installed into the rights and dignity of a theory, and rallied around it, as such, some of the brightest and best minds for three generations.

It was not only faulty in its conclusions, but inadmissible in its steps, and should have incurred the opposition of every intelligent man who understood the limitations of inductive philosophy; but it occupied the vacant space left bare by the labours of Boyle, and, with a growth as luxurious as it was pernicious to the attainment of truth, obstructed in many ways all valuable advance of chemical theory while it lasted.

It may not be amiss, before sketching its rise and overthrow, to point out here wherein its inherent fallacies should have condemned this hypothesis from the outset.

Hypothesis means a guess — a temporary structure erected by the employment of the imagination strictly governed by experience, for the purpose of more rapidly reaching a generalisation than by waiting for all the facts which in the end will be necessary to sustain a full-fledged theory. After one or two facts bearing on a subject are ascertained, it often happens that the mind is directed towards the possible existence of a law which would explain them both; but numerous unknown and untried experiments must result in a certain way in order that this supposed explanation may stand.

With time and a constantly increasing experience more and more such facts are ascertained. If all fall into their places the hypothesis grows stronger and stronger in probability, until, by a large accumulation of such corroborations, the hypothesis passes the undefined line which separates it from theory, and becomes a theory.

This theory then goes on increasing in strength by each additional fact which is found conformable to it, until its convincing force is almost as great to the mind as one of the facts which are the bricks of its construction.

But if, during this period of probation of an hypothesis or of a theory, a single fact is well authenticated which is inconsistent with it, the hypothesis or theory must be abandoned. Of course, in the case of a theory which had been tried and proven hundreds of times, and found to apply to newly-discovered facts, its abandonment would be held in abeyance until every effort had been made to prove the authenticity of the fact and its inconsistency with the supposed explanation; but if these were unalterably confirmed the hypothesis of theory must fall.

This constitutes the true principle of inductive philosophy, and only by pursuing this path rigorously can its processes lead to any good result.

(To be continued).

COTTON-BLEACHING WITH OXYGENATED WATER.

By M. PRUD'HOMME.

THE addition of calcined magnesia to oxygenated water has been recommended for bleaching cotton, but the superiority of the results obtained has not received any explanation. It depends, as I am about to show, on the formation of magnesium peroxide, which at 100° is more stable than hydrogen peroxide.

1. Oxygenated water at 6 volumes, diluted with 10 parts of water, was boiled for half an hour; its standard fell from 1000 to 100.

2. A similar quantity, with the addition of calcined magnesia (5 per cent on the weight of the hydrogen peroxide), falls in strength only to 900.

3. Calcined magnesia is placed in contact with oxygenated water at 3 volumes, at the ordinary temperature. The duration of the contact varies from some hours to many days. It is filtered, washed on the filter, and the product dried at from 100° to 105°.

The determination of the active oxygen by means of a normal solution of potassium permanganate corresponds to the formula $3Mg(OH)_2 + MgO(OH)_2$. This body, by an alkaline reaction, loses all its active oxygen at about 300°.

Magnesium peroxide is also formed on dissolving the metal in oxygenated water. Weltzein considers the product of the reaction a soluble magnesium hydrate. It is easy to show that when evaporated to dryness it gives, with the ordinary tests, the well-known reactions of oxygenated water.

The oxides of zinc and cadmium (metals belonging to the same series as magnesium in Mendeleeff's classification) also give rise to peroxides.

The mixture of zinc oxide and peroxide corresponds approximately to the formula $2ZnO + ZnO(OH)_2$

Cotton bleaching with oxygenated water would remain unintelligible if we confined ourselves to consider it as a simple decolourising agent. It has a direct action upon the different bodies which bleaching has to modify or to eliminate, and even upon cellulose.

Action upon Fatty Bodies.

The saponification of the oils or fats is effected in part by the magnesia, but it is also due to the direct action of the oxygenated water. During ebullition there takes place an abundant liberation of carbonic acid; it may be derived from the oxidation of the glycerin, as it is verified directly. But the oxygenated water, very faintly acid, attacks also the neutral fatty bodies at ebullition, with the liberation of carbonic acid and a formation of fatty acids. These again are transformed by the mixture of oxygenated water and of calcined magnesia, and always with the production of carbonic acid. This happens with the stearic and the oleic acids of commerce. There must occur a partial transformation of this latter body into palmitic acid (as if by the action of potassa lye), for the product of the reaction, if suitably treated with an acid, is richer in soluble fatty acids than the oleic acid of which it forms a part.

The fatty bodies which remain upon the fibre in the state of magnesium oleates, palmitates, &c., are eliminated by a passage in weak acid, followed by an alkaline lye.

Action upon Cellulose.

In bleaching with oxygenated water the cellulose tends to become converted into oxycellulose. This is easily recognised by dyeing in basic colouring matters which fix themselves without a mordant upon oxycellulose.

The modification of the cellulose is more strongly marked if it has been *mercerised*, *i.e.*, saturated with concentrated caustic soda before treatment with oxygenated water. The disaggregation becomes complete, and the tissue becomes a pulp if we add caustic soda to the bath of oxygenated water until it marks 6 to 8° Tw.

The action of oxygenated water upon cellulose is much increased by the presence of certain bodies, such as metallic oxides, which serve merely as a vehicle or intermediate agent for active oxygen. A swatch of cloth mordanted with iron, chrome, or alumina, and boiled with oxygenated water or magnesia for one to two hours, is profoundly attacked at the parts covered by the mordants. It is well, therefore, to let a treatment with weak acid precede the bleaching with oxygenated water, to eliminate the salts or the metallic tissues from the tissue.

The action of oxygenated water and that of cuprammonium upon cellulose present great analogies.

It is easy to show that the ammoniacal solution of copper oxide is an oxidising agent, by allowing it to act upon a

swatch dyed blue with indigo. The solution, if sufficiently diluted to produce no sensible alteration of the tissue, decolourised the blue in 24 hours in the cold, and in a few minutes at 60°. If the cuprammonium solution is sufficiently concentrated to weaken the fibre, this, if well washed and treated with a dilute acid to dissolve out the copper oxide, takes up a full shade on methylene blue : there is therefore a formation of oxycellulose.

A swatch of cotton cloth mercerised in caustic soda at 36°, and thoroughly washed, is left in contact for some hours with a cuprammonium solution of medium concentration. The fibre is more attacked than that of a check swatch which has not been mercerised.

We conclude from these experiments that, contrary to the received opinion, cellulose is attacked and transformed by contact with the reagent of Schweitzer.—*Comptes Rendus* (cxii., p. 1374).

NOTICES OF BOOKS.

Researches on Cobalt. An Inaugural Dissertation submitted to the Philosophical Faculty of the Univerity of Erlangen. By HUGO REMMLER. (Untersuchungen über Cobalt. Inaugural Dissertation zur Erlangung der Doctor Wuerde bei der Lohen Philosophischen Fakultät der Universität zu Erlangen). Berlin : Dobrin.

THE author points out the discrepancies in the determinations of the atomic weights of cobalt and nickel as obtained by chemists of recognised standing. He quotes a table from the work of Cl. Zimmermann, in which the results vary in case of cobalt to 2·09 per cent of the total, *i. e.*, from 59·87 to 58·57. In order to ascertain the cause of discrepancies, the more unsatisfactory as both cobalt and nickel have been made the subject of repeated examinations, he attacked a large specimen of the purest cobalt to be procured by the process of fractionation. By digesting cobaltic hydroxide for about nine months in aqueous ammonia, he obtained twenty-five extracts, twenty-four of which, after purification, were purified, and their atomic weights were determined. The values obtained ranged from 59·531 to 58·299.

All the preparations had been purified in exactly the same manner. It is to be remarked that the atomic weights found did not increase or decrease progressively. This fact seems to point to the conclusion that cobaltic hydroxide is either a compound or a mixture of two hydroxides, each of which is unequally soluble in the liquids employed. The author's results, therefore, seem to agree with the result of Krüss and Schmidt, that cobalt purified by the ordinary methods contains two components of different atomic weights.

Catalogue of Standard Second-hand and New Books, English and Foreign, on Chemistry and the Allied Sciences, Technology, &c., Offered by WILLIAM F. CLAY, 2, Teviot Place, Edinburgh.

THIS catalogue will be, we feel sure, of great interest to our readers. It is especially rich in sets of Journals and Transactions which are becoming increasingly scarce and difficult to procure. Thus we find here quotations of the *Analyst*, complete, from the beginning to 1886 ; the *Annalen der Physik* (Gren and Gilbert's), from 1792 to 1824 ; the *Cavendish Society's Publications*, complete ; the *Journal of the Chemical Society*, from 1863 to 1890 ; the *Journal fur Praktische Chemie*, from the commencement to 1860 ; the *Berichte der Deutschen Chemischen Gesellschaft*, from 1883 to end of 1889 ; the *Chemiker Zeitung*, 1881 to 1888 ; the *Comptes Rendus*, vols. i. to c., and various other important series, to which the librarians of scientific societies, colleges, &c., should have their attention directed. We find also odd volumes, which may often be required for completing sets.

There are many choice works from the library of the late Prof. Carnelley. There is a complete set of the *Pharmaceutical Journal* and *Transactions* from the outset to 1889, a series very difficult to procure complete.

As an instance of the reasonable character of the prices we find that the *Encyclopedie Chimique*, edited by Frémy, a work only completed last year and published at £60, is now offered for £25 !

CORRESPONDENCE.

THE RELATION BETWEEN THE CHEMICAL CONSTITUTION OF CERTAIN ORGANIC COMPOUNDS AND THEIR ACTION UPON THE ULTRA-VIOLET RAYS.
(A CORRECTION.)

To the Editor of the Chemical News.

SIR,—In your last issue Prof. W. N. Hartley points out that Dr. Krüss, in his memoir entitled "Beziehungen Zwischen Zusammensetzung und Absorption-Spektrum organischer Verbindungen," which appeared three years ago in the *Zeitschrift für Physikalischen Chemie*, has attributed to me conclusions drawn from an examination of the action of certain organic compounds on the ultraviolet rays, which in reality were drawn by Prof. Hartley himself, in a series of papers which are well known to every English worker. I much regret that this is the case, and I am anxious to do whatever lies in my power to correct the error into which Dr. Krüss has undoubtedly fallen. At the same time, however, I must take very decided exception to the inaccurate and misleading account which Prof. Hartley has given of the facts of the case, and especially to the suggestion that I am in any degree responsible for the confusion. As far as I am concerned the facts are as follows.

Eleven years ago, when I was Demonstrator of Chemistry at the Pharmaceutical Society, I carried into operation a plan by means of which my advanced students might be kept aware of the progress which was being made in the various branches of chemical science. The plan was carried out in connection with a Students' Association which is attached to the Pharmaceutical Society's School. Certain members were appointed to report, from time to time, on recent chemical work. I undertook to deal with Organic Chemistry, and in July, 1880, now exactly eleven years ago, I made a report on the work done by Miller, Soret, and more recently by Hartley and Huntington, in tracing the connection between the chemical constitution of organic compounds and their action on the ultra-violet rays. The substance of this report, which took the form of a lecture, subsequently appeared in the *Pharmaceutical Journal* of July 17th, 1880,—not, however, in the portion of that journal which is devoted to original communications, but in the later portion in smaller type, and as a part of the account of the proceedings at the last meeting of the Students' Association. No one who read this report could possibly be under any misapprehension as to its character. Although the lecture was designedly a popular one, yet in the substance of it which appeared in print it was made quite clear that the experimental work had been done, and the deductions from it had been drawn by Messrs. Hartley and Huntington, whose names were duly mentioned, as were also the references to their original memoirs, which had been consulted in preparing the report.

From what I have written it will, I think, be clear that neither in the substance of my lecture nor in the mode of publication of the abstract of it was there anything likely to give a false impression as to my connection with the subject. A large number of similar reports have since appeared in more or less detail in the *Pharmaceutical*

Journal to the manifest advantage of advanced students connected with the Society, but, so far as I am aware, the present case is the only one in which confusion has arisen.

The annoyance which Dr. Krüss's mistake has quite naturally caused Prof. Hartley has, I am afraid (even after the lapse of three years), led him to make certain unwarrantable assertions which I feel compelled to refute.

Prof. Hartley asserts that Dr. Krüss has been misled into assigning to me priority in respect of this research on account of my lecture having dealt with results which Prof. Hartley did not actually publish until some months after the appearance of the abstract of the lecture. Prof. Hartley states that " by this report being quoted and referred to as an original contribution I also was misled and put to the trouble of consulting it. I then found that it was published actually prior to my papers entitled " Researches on the Relation between the Molecular Structure of Carbon Compounds and their Absorption Spectra," for although they had been verbally communicated to the Chemical Society as early as June, 1880, and in writing on December 2nd of the same year, they were of necessity not published in the Journal until March, 1881, while Prof. Dunstan's report on them appeared in January. He thus appears to be entitled to priority in respect of these matters." As a matter of fact the assertions and implications here made are absolutely without foundation.

In the preparation of my lecture I used no information which had been published by Prof. Hartley later than June, 1880. As appears from the footnotes in the abstract of my lecture, the original memoirs were carefully consulted and I did not " merely make use of abstracts of them." Lastly, I would point out that my lecture did not appear in January, 1881, as Prof. Hartley asserts, but in July, 1880, so that it could not possibly have dealt with facts which Prof. Hartley did not publish until the following year (1881).

I think I have now gone into sufficient detail to show how inaccurate the premises are from which Prof. Hartley has concluded that I am responsible for my " report being quoted and referred to as an original communication."

Since reading Prof. Hartley's letter, I have been considerably puzzled to understand how it has happened that my lecture has been dragged out of its original obscurity and " referred to as an original communication." I cannot find that the lecture was abstracted in any scientific periodical, and it is not likely that Dr. Krüss would naturally refer to the reports of the meetings of the School of Pharmacy Student's Association, which appear in the *Pharmaceutical Journal*, for information on such a subject, unless, indeed, his attention were specially directed to them.

In considering the different means by which prominence might have been accorded to my lecture, it occurred to me to refer to the bibliography of spectrum analysis drawn up by a Committee of the British Association in 1881, and there (York Report, 1881, p. 415) I was surprised to find the abstract of my lecture " quoted and referred to as an original communication," and my astonishment was considerably increased when I observed that Prof. Hartley was a member of the Committee which compiled this list of papers.

It is now clear upon whom rests the responsibility for Dr. Krüss's mistake. As, however, I am anxious that the confusion which Prof. Hartley assisted in initiating should as far as possible be obviated, it is my intention to address to Prof. Ostwald—the editor of the *Zeitschrift für Physikalischen Chemie*—for insertion in his journal, a note, pointing out that my communication, to which Dr. Krüss has referred, is not an original contribution, but merely the substance of a lecture on recent advances in this department of physical chemistry ; and that the conclusions he has attributed to me were drawn

by Profs. Hartley and Huntington, and published by them some time previous to the delivery of my lecture.—I am., &c.,

WYNDHAM R. DUNSTAN.

Research Laboratory,
Pharmaceutical Society of Great Britain,
London, June 29, 1891.

MISLEADING TITLES.

To the Editor of the Chemical News.

SIR,—The subjoined letter appeared in *The Standard* of Friday, June 26th, 1891.

If the Royal Society can do this, why cannot the Chemical Society ?—I am, &c.,

PUZZLED.

SIR,—The attention of the President and Council o the Royal Society has been called to an advertising pamphlet, the title-page of which states that it is by Professor Harley Parker, F.R.S.

As the letters F.R.S. are used to denote that the bearer of them is a Fellow of the Royal Society, and as there is not, and never has been, a Fellow of the name of Harley Parker, I have been directed to request you to call public attention in your paper to this misuse of the initials F.R.S. The public will be able to judge of the intention with which they have been wrongfully assumed. —I am, Sir, your obedient servant,

HERBERT RIX, Assistant Secretary to the Royal Society.

The Royal Society, Burlington House, June 25.

ESTIMATION OF TANNIN.

SIR, — I should feel much obliged if you could give enclosed circular the publicity of your columns, as there may be many chemists who are interested in the matter whose names I do not know.—I am, &c.,

H. R. PROCTER.

Leather Industries' Department,
The Yorkshire College, Leeds, June 25, 1891.

In view of the serious discrepancies which often occur in the percentages of tannin found in gambier by different chemists, I have been requested by the Leeds Leather Trade Association to act in conjunction with Mr. R. G. Salomon, of Newark, N.J., Chairman of a Committee of the National Morocco Manufacturers' Association of the United States, to collect information with a view to the adoption by the two associations of a uniform standard method for the analysis of gambier. There seems no doubt that there is a very strong consensus of opinion in favour of the indirect gravimetric method, in which equal portions of the infusion of the tanning material are evaporated, in the one case after careful filtration through paper only, and in the other after the complete removal of the tanning matter by treatment with purified hide-powder ; and the tanning matter is calculated from the difference of weight of the dried residues. I shall be glad, however, to receive any suggestions you may be good enough to make, either as to the general method to be adopted, or the details of preparing the infusion and absorbing the tannin, which are matters of considerable importance.

I am sending this circular to a number of chemists who are interested in the question : and I propose, before reporting to the Associations, to embody the information I receive in a paper for the Society of Chemical Industry, so that the matter may be verbally discussed at the different sections, and the prevailing opinion fully ascertained, as it is very desirable that a uniform method should be unanimously adopted.

HENRY R. PROCTER.

June 23, 1891.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxii., No. 24, June 15, 1891.

On Ferro-carbonyle: A Volatile Compound of Iron and Carbon Monoxide, and on Nickelo-Carbonyle.—M. Berthelot.—Iron in a certain state combines directly, and in the cold, with carbon monoxide. The iron is obtained by reducing ferric oxide (precipitated, washed, and dried with care) in a slow current of hydrogen at the lowest temperature possible. The reaction of carbon monoxide with iron thus prepared takes place at about 45°. The product is a gas. The author has re-examined the nickelo-carbonyl discovered by Mond, Lang, and Quincke, which is a liquid, boiling at about 46°. It is not appreciably absorbed either by water, dilute acids, or alkalis, or acid cuprous chloride. Its true solvent is the essential oil of turpentine. Carbon monoxide has thus the property of uniting in the cold with nickel, iron, and doubtless with other metals taken in a suitable condition. It forms thus an order of special compounds, analogous to compound metallic radicles. These compounds are capable of oxidation and of other reactions, forming complex organic compounds. From another point of view a compound of iron with carbon monoxide doubtless plays a part in various reactions observed in metallurgy, such as the precipitation of carbon from carbon monoxide in contact with iron, observed by Gruner; the formation of gaseous bubbles in the midst of softened iron, observed by Cailletet, &c. Certain transfers of matter observed either in cementation-pots or in Siemens furnaces are also connected with the existence of ferruginous compounds of this nature.

Researches on the Application of the Measurement of the Rotatory Power to the Determination of the Combinations formed by the Aqueous Solutions of Mannite with the Acid Sodium and Ammonium Molybdates.—D. Gernez.—The author has previously demonstrated that the solutions of active tartaric and malic acids when brought in contact with the aqueous solutions of inactive bodies, such as the molybdates, phosphomolybdates, tungstates, &c., form compounds which exert upon polarised light an action which is a number of times greater than that of the active body which they contain. He has now found that other active bodies which have not a double function (acid and alcoholic) lend themselves to a similar study. His observations have been in the first place made with mannite.

On Quinethyline: A Base Homologous to Quinine.—MM. E. Grimaux and A. Arnaud.—They give the generic name quinines to compounds of the general formula $C_{19}H_{21}N_2OOR$, R being any group whatever. The first term of the series is quinomethyline, or ordinary quinine, and the second term is quinethyline, a substance which they describe in the present paper. Its composition is $C_{21}H_{26}N_2O_2$.

On the Ureides derived from Normal Acids.—M. C. Matignon.—The author has obtained formylurea and acetylurea. Their formation heats are respectively equal to 119·3 cals. and 129 cals.

Method of Formation of the Methylcamphocarbonates of Methyl and Ethyl. Preparation of Methylated Camphor.—J. Minguin.—Not adapted for useful abridgment.

Nitrosocyanacetic Ethers.—P. Th. Müller.—The author obtains these ethers by causing amyl nitrite to act upon the sodium-cyanacetic ethers.

Bleaching of Cotton with Oxygenated Water.—M. Prud'homme.—(See p. 9).

Synthesis in the Group of Sugars.—E. Fischer.—A portion of a memoir inserted in the *Berlin Berichte,* vol. xxiii., p. 2114.

Limited Reactions.—M. Prud'homme.—A purely mathematical paper, incapable of abridgment.

Action of Mineral Acids in Saccharification by Malt and the Fermentation of Starches.—Dr. J. Effront.—In this chapter of his memoir the author considers the influence of hydrofluoric acid and of fluorides in the fermentation of amylaceous matters. He states that whilst in ordinary fermentations the yield of alcohol was only 43 per kilo. of starch, by the use of fluorides it is raised to 61·9.

On Recent Colouring Matters.—F. Reverdin.—The author mentions the oxidations of orthophenylenediamine effected by O. Fischer and E. Hepp; the combination of α-β dinaphthylamine with diazobenzine, by P. Matthes; the azo-colours containing the quinone group, by Dr. F. Kehrmann (*Chem. Zeit.*); the transformation of acetone-oxalic ether into symmetric oxytoluylic acid, by L. Claisen (*Berichte*); and the synthesis of chrysene and the accompanying hydrocarbons, by Kraemer and Spilker (*Berichte*).

Alkaloids, Pharmaceutical Products, Essences, and Extracts.—Notices of the mixture of furfurol and methylfurfurol known as fucusol (*Leibig's Annalen*); of the phenole of oil of sassafras, by C. Pomeranz (*Monatshefte der Chemie*); on orthine, a novel hydrazinic derivative proposed for use as a febrifuge (*Pharm. Central Halle*); the examination of phenacetine, by J. Luttke (*Pharm. Central Halle*); on aristol—an iodine compound of thymol used by Dr. Eichhoff in the treatment of skin diseases (*Pharm. Central Halle*); the composition of gum tragacanth, which according to Prof. Maisch (*Romieu's Journal*), is:—

Moisture	..	.. ..	18·92
Soluble gum..	..	..	35·94
Insoluble gum	..	..	43·39
Ash	.. ..	.. ..	2·27
			100·00

starch being totally absent; on the essential oil of betel, by Dr. J. F. Eykman (*Berlin Berichte*); composition of the seed of *Calycanthus glaucus,* a rosaceous plant common in Georgia, and the *Cardinas,* very poisonous to cattle (*American Chem. Journal*); the solanidine of potato shoots, by Jorissen and Grosjean (*Acad. Royale de Belgique*); the formation of hydrogen peroxide at the expense of ether, by W. R. Dunstan and T. S. Dymond (*Journal of the Chem. Society*); quantitative separation of strychnine and brucine, by J. E. Gerock (noticed under *Zeit. Anal. Chemie*); determination of benzoic aldehyd in bitter-almond water, by C. Denner (*Pharm. Central Halle*).

Review of Photography.—This consists of a lengthy memoir on "orthochromatism" in photography, on toning Eastman's paper by means of platinum and magnesium chloride, the elimination of hyposulphite, the preparation of ferric oxalate, toning with aristotype paper, and on negative varnish.

The Manufacture of Potassium Ferrocyanide.—Mr. Readman.—From the *Journal of the Society of British Industry.*

Affinity of Heavy Metals for Sulphur.—(*Wissen. Wochenschrift.*)—Insoluble sulphides are able to precipitate other metals from solution in the state of sulphides whilst becoming themselves soluble. Thus, copper sulphide with a solution of silver nitrate gives a precipitate of silver sulphide. Silver, therefore, has more affinity for sulphur than has copper. In 1837 Anthon drew up a table of the metals in the order of their decreasing affinity

for sulphur. Silver comes first, then follow copper, lead, cadmium, iron, nickel, cobalt, and manganese. E. Schürman has resumed and enlarged the researches of Anthon. He arranges the metals as follows :—Palladium, mercury, silver, copper, bismuth, cadmium, antimony, tin, lead, zinc, nickel, cobalt, iron, arsenic, thallium, manganese. The saline solution of a metal of this series may be decomposed (at least in great part) by the sulphide of any of the following metals, *i.e.*, the metals following in the above list. The decomposition is so much the more complete as the metals are more remote from each other in the series. The metals at the head of the series are those which have the strongest affinity for sulphur. This affinity decreases insensibly until we arrive at manganese, which has very little. Manganese sulphide is decomposed by the saline solutions of all the foregoing metals.

Vulcanisation of Caoutchouc: A Special Study on the Use of Sulphur Chloride.—C. A. Fawsitt (*Dingler's Journal*).—The author proposes, instead of free sulphur or antimony sulphide, the use of which requires an elevated temperature, to employ sulphur chloride dissolved in carbon disulphide. The materials must be pure ; the carbon disulphide must contain neither free sulphur nor fatty or tarry substances. The author has patented another process, in which the sulphur chloride is employed without solvent in the state of vapour.

MISCELLANEOUS.

Wanklyn's " Water Analysis."—The issue of the eighth edition of this book moves me to put on record a slight historical sketch which perhaps may interest some of the readers of the CHEMICAL NEWS. The book may be said to owe its origin to the late Mr. Brayley, who was librarian to the London Institution when the Laboratory of the Institution produced the ammonia process. I had published the ammonia process of water analysis in my evidence given before a Royal Commission sitting in the House of Lords, and also in a paper read to the Chemical Society in 1867, and yet Mr. Brayley assured me that that would count for nothing unless I would write a book on the subject. Mr. Brayley was wise in his day and generation, and he was a librarian. I submitted, and with great reluctance sat down to write the first edition of the water-book, which was published in the spring of the year 1868. The book, which, by the way, was brought out at my risk, yielded a slight profit, and in 1870 a second edition was required. That edition —the Chapman edition—was edited by the late Mr. Chapman, who perished in an explosion of nitrate of methyl in a German factory, about a year after the issue of the second edition. In 1874 the third edition was called for, and with the advantage of seven years' practical experience of the ammonia process I re-cast the book, which then assumed its present shape. The reception of the third edition was most flattering to its author. The book was authoritatively declared to be a text-book on the subject. Since that time I have scrupulously maintained the integrity of the text and the essential part of the book, the section entitled Water Analysis for General Sanitary Purposes has come down to the present year without any textual alteration, except extension due to the insertion of the moist combustion process and a little amplification of the classification of drinking waters, on page 68. It is, indeed, true that since 1874 the book has increased considerably in thickness ; but that is mainly owing to the development of the non-essential portions. The eighth edition, just sent out by the publishers, is an absolute re-issue of the seventh edition, all except one-half of page 54, which contains certain explicit directions for the working of the moist combustion process.—J. A. WANKLYN.

THE CHEMICAL NEWS.

VOL. LXIV., No. 1650.

ON THE

DETERMINATION OF THE AMOUNT OF FATTY MATTER PRESENT IN OLEINE (TURKEY-RED OIL).

By ROWLAND WILLIAMS, F.I.C., F.C.S.

DURING the last few years I have made a large number of analyses and experiments with the view of testing the accuracy of some of the methods which have been proposed from time to time for the estimation of the total fatty matter (fatty acids and glycerides), present in Turkey-red oil, or oleine, to use the name by which it is known commercially in this district.

It would answer no useful purpose, besides being extremely tedious, to describe every detail of the investigation referred to above, so I content myself with giving a brief summary of the main results obtained. For convenience sake the methods in general use may be divided into three groups :—1. Volumetric methods in which the volume of fatty matter resulting from the decomposition of a known quantity of oleine is ascertained and the percentage calculated therefrom. 2. Methods depending upon the use of some volatile immiscible solvent (such as ether or chloroform), for dissolving the fatty matter from a weighed portion of the sample, after decomposing with acid, and subsequent evaporation of the volatile solvent and weighing the fatty residue. 3. What is usually termed the " wax " method.

1. The volumetric method in some form or other is used by most manufacturers of oleine for the valuation thereof, and it is also in vogue in many dyeworks and printworks where the strictest accuracy is not required, as such a method is considered by many to be sufficiently exact for technical purposes. All the volumetric methods which I have met with for the determination of fatty matter in oleine are, however, distinctly wanting in scientific precision, for reasons which I shall explain presently. Originally, the volumetric method was carried out somewhat as follows, although various slight modifications have been introduced since by different operators :—A weighed quantity of the sample is placed in a graduated cylinder or other suitable apparatus, and, after decomposing with acid, with application of heat, the fatty matter is eventually read off and calculated to percentage. This is, of course, the process in its simplest form, and is obviously capable of considerable improvement. Whenever I have occasion to employ the volumetric method I use flasks of rather more than 5000 grains capacity, which I had made specially for the purpose. The necks of the flasks are moderately narrow, and are carefully graduated into 100 divisions, each representing five grains. I weigh some 400 or 500 grains of the sample (if that quantity be available), direct from a beaker into the graduated flasks, add a little dilute acid and some saturated salt solution and heat in a boiling water-bath for a short time, finally adding hot salt solution until the fatty matter rises to the graduated part of the neck. When cold, the fatty layer can be read off with a fair degree of accuracy, and is calculated *directly* to percentage. Several objections to this method will suggest themselves at once to anyone who has had much experience in the matter, but the gravest defect is, in my opinion, the confusion between weight and volume, which seems an inherent part of the process. As the specific gravity of the fatty layer varies in different samples of oleine, even when made entirely from genuine castor oil, it would obviously be difficult to make a correction ; anyhow, to the best of my knowledge

this is never done. My experience of the volumetric method just described is that it almost invariably yields results from 2 to 4 per cent in excess of the truth, hence, I presume, the considerable degree of favour which it enjoys among manufacturers of oleine.

2. The ordinary way of applying this method consists of decomposing a weighed quantity of the sample with acid and then shaking with some volatile solvent (generally ether), in a separating funnel. The solution of the fatty matter is run into a weighed flask, the volatile solvent evaporated, and the fatty residue dried at the lowest temperature practicable. This method is theoretically an excellent one, but in practice I have found it somewhat unsatisfactory, owing to the fact that a certain amount of water and saline matter are always retained by the ether, rendering the drying of the fatty matter a difficult and tedious operation, besides necessitating a determination of the mineral matter in many cases. The following modification has been suggested by J. A. Wilson (*Journal of the Society of Chemical Industry*, vol. x., p. 28) :—" 10 c.c. of perfectly saturated salt solution are pipetted into a globular separator of about 100 c.c. capacity, and from five to six grms. of the sample poured directly into the separator. About 5 c.c. of HCl1−2 is then added and the whole thoroughly agitated, after which about 50 c.c. of ether is added and again agitated. The ethereal layer is received into a dry flask, and the aqueous layer again agitated with about 25 c.c. ether, which is received in the flask with the first extract. The ether is then evaporated and recovered, and the fatty matter in the flask dried by blowing dry air through about ten minutes. From 25 to 35 c.c. of really absolute alcohol is then added, agitated, and allowed to stand a short time, poured through a dry filter, the residue in flask washed two or three times by alcohol, and the filtrate and washings received in a tared flask, the alcohol evaporated, and the residue kept on the water-bath about one hour, whilst a current of purified air is continuously passed through the flask. The residue is then weighed and the percentage calculated." At first sight this method seems rather ingenious, but on putting it to the test upon several samples of oleine which have been sent to my laboratory for analysis lately, I found it to yield unsatisfactory results, invariably below the truth. I have arrived at this conclusion after making a considerable number of analyses and experiments, and my opinion is confirmed by the chemist in a well-known printworks in this district. The low results are, I believe, mainly due to decomposition of the fatty matter during the process of drying, but there are other possible sources of error. After the meeting at which the paper was read I called Mr. Wilson's attention to the danger of drying the fatty residue on the water-bath for so long a period as an hour, as decomposition would be certain to ensue to a greater or lesser extent. Mr. Wilson then informed me that he sometimes dried the fatty matter *in vacuo*, but as no mention is made of this in the published directions (which I have quoted verbatim), it would appear that he does not attach special importance to the point in question. Mr. Wilson seems to have made one very serious mistake in connection with this method. Like Mr. Guthrie, who published a new process for the estimation of fatty acids in alizarin oil last year (CHEMICAL NEWS, vol. lxi., p. 52), which I subsequently criticised and proved to be inaccurate (vol. lxi., page 76), Mr. Wilson seems to have made no effort to substantiate the accuracy of his method, but is apparently content to bring it forward mainly on account of certain novel features which it undoubtedly possesses. Before publishing a new process, or a modification of an old one, I consider it of the first importance that a chemist should employ every means in his power to verify its accuracy.

3. The " wax method," some form of which has been employed for a good many years, has now been adopted by nearly all the leading professional chemists as the most reliable for the determination of fatty matter in oleine. It has

been subjected at various times to a considerable amount of hostile criticism, and there is no doubt that in the hands of an inexperienced analyst the " wax method " is liable to give misleading results. On the other hand, when suitable precautions are taken by an expert in this branch of commercial analysis, I am convinced that no process can be more satisfactory. It is exceedingly simple —probably more so than any other gravimetric process we have for this purpose, and does not occupy an undue length of time in execution. The following is a description of the " wax method " as used in my laboratory :— Weigh 200 grains of the sample into a small porcelain basin, add 50 grains dilute hydrochloric acid (10 p.c.), and 300 grains saturated salt solution, then warm gently for a few minutes, add 200 grains white wax, and heat until the whole is perfectly liquid. Let cool, preferably for some hours, so as to allow the cake of wax and fatty matter to set as firmly as possible. Next, lift the wax, &c., out of the basin and wash the latter till all the salt is removed, and dry the basin thoroughly. Wash the cake of wax, &c., first with saturated salt solution, then with the smallest possible quantity of *very cold* water. It is advisable to pour the original fluid from the basin and also the washings into a clean beaker, in order to see whether any traces of fatty matter eventually rise to the surface. If not, it may be taken for granted that all the fatty matter from the 200 grains of the sample is adhering to the white wax. It is at this point that special care and experience are necessary, as the accuracy of the results depends almost entirely upon the manipulative skill with which the cake of fatty matter is now treated. The cake is dried as gently as possible (especially the under surface), by means of absorbent paper, and finally rendered perfectly dry either by leaving in a desiccator over sulphuric acid for some time, or by gentle heating accompanied by constant stirring. I have found the latter plan to answer equally as well as the former, provided that the temperature be not allowed to exceed 160° F. The basin and contents are allowed to cool and then weighed. On subtracting the weight of basin and wax from the total weight and dividing by two, the percentage of fatty matter is obtained. I have described the " wax method" with what may perhaps seem unnecessary detail, but this is not really the case. On the contrary, it is only by paying the strictest attention to all the little points which I have mentioned, together with constant practice in this class of analysis, that accurate results can be obtained. It is, indeed, probably inattention to detail and want of experience which has caused the " wax method " to be condemned as unreliable by certain chemists.

I have tested the " wax method " described above on three samples of oleine prepared by myself with extreme care from castor oil obtained from altogether distinct sources. The results obtained were very satisfactory, being, in fact, almost identical with theory in two out of the three samples. In the accompanying table will be found the figures yielded by a number of samples of oleine which I have examined during the last few months, by the methods referred to in the course of this paper. I think these will be sufficient to show the undoubted superiority of the " wax method."

Oleines.

Samples prepared by myself.	"Wax Method."	"Volumetric Method."	"Wilson's Method."
No. 1 (50 p.c.)	49·86	55·19	48·56
,, 2 (61·36 p.c.) ..	61·58	64·28	58·87
,, 3 (70 p.c.)	69·92	73·88	66·77
Samples received for analysis.			
No. 1	47·41	49·48	45·25
,, 2	67·92	72·22	65·85
,, 3	48·40	52·73	46·12
,, 4	44·44	47·10	43·10
,, 5	68·98	72·15	66·56
,, 6	49·50	52·35	47·70

While not claiming special originality for the contents of this paper, I do claim to have proved that the " wax method," if carried out *exactly* as I have indicated, may be relied upon to yield more accurate results than any other which has been published hitherto for the determination of fatty matter in oleine. It is worthy of note that many dyers and calico-printers decline to accept results obtained otherwise than by the " wax method."

I cordially invite criticism from makers and users of oleine and from others interested in this important subject, and shall be glad to consider any suggestions or possible improvements in the methods which may be brought forward.

Laboratory and Assay Office,
28, Pall Mall, Manchester.
   July 1, 1891.

THE FARADAY JUBILEE.

IN commemoration of the centenary of Faraday's birth, which occurs this year, two lectures have lately been given at the Royal Institution by Lord Rayleigh and Professor Dewar. We hope to publish these lectures in full before long. In the meantime we think it may interest our readers if we print a letter received from an old friend, long since dead, to whom the Editor wrote asking for his assistance in preparing an obituary notice for the CHEMICAL NEWS, on the occasion of Faraday's death. The following letter, received in reply, is as good a memorial of the illustrious dead as any that could be written at the present day :—

Cornwall, August 30, 1867.

DEAR CROOKES,—I should be proud indeed to be the spokesman of the chemical world in doing honour to Faraday's illustrious name on the occasion of his accession to immortality. But I should not dare to meddle with the laurels on so august a brow, without many days and nights of earnest research and meditation, to fit me for summing up, without omission, the splendid list of his imperishable labours.

Only in this reverential spirit of earnest solicitude to do aright, which is, if I mistake not, the philosophical counterpart of prayer—of the religious feeling—could so solemn a duty be fitly undertaken.

Only with the aid of other minds, kindred with Faraday's in genius, and filled with the light of his manifold discoveries, could any one man's mind become an adequate mirror to reflect the gigantic Shadow that has just passed to its place in futurity.

For the present it is my fate to fulfil much humbler duties,—which, having undertaken, I have no right to set aside. For duty must still be done, even when such appeals as yours set the wings of the caged lark trembling, and point him upwards to his barred out home.

I must remain, therefore, a unit among the millions whose hearts do silent homage to the illustrious dead,—and can but watch, from afar, the starry coronation of which you invite me to be minister.

So best, perhaps. For, after all, the name and fame of Faraday transcend all pomp of celebration, all burning words of praise. For whose the pen to weave so bright a glory as that Electric fire which glows, through all the ages, round his brow, who first drew lightning from the lodestone as Franklin drew it from the sky ?

In the moment of separation that little spark breaks forth—instantaneous, yet eternal. It is but one vivid point of the radiance that encircles his name, yet of itself it is glory enough.

From that spark a new branch of science has sprung; and under its creator's name, were it mine to carve his epitaph, these three should be the chosen words,

FULMEN ERIPUIT FERRO !

—Ever yours, faithfully,

F. O. WARD.

THE FORMATION OF STARCH FROM FORMALDEHYD.

By TH. BOKORNY.

THE author assumes that formaldehyd is formed by the reduction of the carbonic acid on chlorophyll, and that carbohydrates (starch) are then produced by its condensation. Experiments made with pure formaldehyd to effect the formation of starch on the chlorophyll-organs of Algæ miscarried on account of the poisonous action of this substance. Experiments with methylal, which easily splits up into methyl-alcohol and formaldehyd, were more successful as the formation of starch was ascertained. Still the results of these experiments were ambiguous, as the starch which was detected might have been formed from methyl alcohol.

Recently the author has experimented with sodium oxymethyl sulphonate, which is readily broken up into formaldehyd and acid sodium sulphite :—

$$OH.CH_2.SO_3Na = CH_2O + HSO_3Na.$$
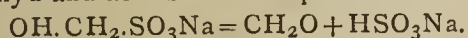
Carbohydrates are formed from the formaldehyd by condensation, $(CH_2O)_6 = C_6H_{12}O_6$.

In order to prevent the injurious action of the primary sodium sulphite set free in the decomposition, di-potassium or disodium phosphate was added to the solution, which converted the acid sulphite into a neutral sulphite, with the simultaneous formation of a monophosphate.

The author placed Algæ (*Spirogyra majuscula*) in a culture-solution containing 0·1 per cent of sodium oxy-methyl-sulphonate and 0·1 per cent K_2HPO_4, and allowed them to remain in air free from carbon dioxide with varying illumination. After five days enormous quantities of starch were found in the Algæ. Even in six hours starch could be demonstrated in Algæ which had been previously freed from starch.—*Deutsch. Gesell. Berichte* and *Chemiker Zeitung.*

THE PROGRESS OF CHEMICAL THEORY: ITS HELPS AND HINDRANCES.*

By Dr. PERSIFOR FRAZER, Prof. of Chemistry.
(Continued from p. 9).

THE obvious difficulty of the phlogistic theory was that the calx, which was considered the simple body, was heavier than the metal which was supposed to be the compound, and this circumstance was explained by supposing that the phlogiston which was absorbed from the fire when the calx was heated therein had the principle of "levity" as opposed to that of "gravity," and that the more of it which was collected in a body the lighter became that body.

Here was the unpardonable error of the phlogistonites in the defence of their theory.

Hofmann (1660—1742), the first to distinguish between magnesia and alumina, asked whether, instead of the above explanation of combustion, it was not the case that a metal received an "acid" when burned, which "acid" was re-absorbed when the metal was reduced. Besides him many others had noted the increase of weight n combustion, and Boerhave (1668—1738) had doubted the explanation above referred to.

The offence of which, as seekers after truth, the phlogistonites were guilty was that of calling into existence a substance which was diametrically different in its properties from any then known, and making this imaginary substance and its purely imaginary properties the basis of a theory.

Isaac Newton (1642—1727) had established, by his matchless investigations, commencing 1666, the nature and properties of matter, one of which, gravitation, was common to all bodies, and there was no excuse for an

hypothesis, after that date, which should deliberately rob matter of its one all-pervading attribute, unless some discovery had been made which seemed to support it.

If it be said that the observations on the combustion of bodies seemed themselves to furnish this proof, it must be admitted that for such an overthrow of all that had been patiently built up, some independent testimony unconnected with the then obscure phenomena of combustion ought to have been sought. This was an unpardonable deflection from the line of calm and dispassionate inquiry, and deserves to be held up for all time to the condemnation of scientific men as a warning, and its fate as an example,—the more so because as time went on, and the array of obstacles to the acceptation of this theory increased, its supporters were obliged to set up one after another distinct hypotheses to support the first untenable one, until the discussion partook more of the nature of those verbal juggles popular among the schoolmen of the Middle Ages than the efforts of students of Nature to arrive at a knowledge of her laws.

Marggraf (1709—1783) introduced into chemistry the study of reactions in the wet way, and thus laid the foundation of analytical chemistry. He recognised soda as an alkali, and magnesia and alumina as peculiar earths. Against the opinions of his predecessors he held that ammonia was not produced in the distillation of wood, &c., by the union of its constituents, but that it pre-existed in the wood.

J. Black, of Scotland, by his investigation of the alkalies, dealt the first serious blow to the phlogistic theory. He found that magnesia could be changed to "mild" from having been strongly alkaline, by exposure to air or by contact with "mild" alkalies. In other words, that it became carbonate of magnesia by exposure to the carbonic acid of the air or by treatment with the carbonates of the alkalies. Furthermore, he showed that what it lost or gained in these changes was a gas like air, which separated from it under treatment by acids with effervescence, whereas in its caustic condition acids dissolved it without effervescence. He also, with singular astuteness, established for his theory of combustion (which was to finally take the place of the phlogistic theory) the principle of latent heat. The immediate result of Black's discoveries was the rise of pneumatic chemistry or the chemistry of the gases.

Joseph Priestley (1733—1804) followed with more success than any other this line of investigation. He worked sporadically and without system, but with wonderful penetration discovered many things that had escaped the attention of better chemists. He himself called his achievements "sportsman's luck." He found the nitrogen left after combustion in air, and determined its proportion by volume. He regarded it as charged with phlogiston.

In 1774 he discovered oxygen in the oxide of mercury, and, recognising it as the supporter of combustion in the air, made it the measure of the destruction or devitalisation of the air. He discovered, besides oxygen and nitrogen, the reduction of the calxes by hydrogen. He also observed that by the passage of the electric spark through confined air in contact with moistened litmus, a new acid was produced which coloured the latter red, He furnished more material than any other chemist of the day for the destruction of the false phlogistic theory, but he was not only incapable of correctly reasoning on the facts which he had brought to light, but to the day of his death he maintained that his pivotal discovery, the corner-stone of the chemistry of to-day (as it was made by Lavoisier), was nothing but the production of dephlogisticated air.

It was a touching thought for those of us who, in 1874, assembled at his grave in Northumberland, Pa., to do honour to his memory as a great discoverer and a devoted friend of our young States when we threw off the English yoke, and to celebrate the centennial anniversary of the foundation of modern chemistry, in his isolation of

oxygen, that this great mind, so potent in the discovery in the science which he adorned, rejected the obvious fruits of that discovery, and insisted on rejecting the honour which should justly have been his.

H. Cavendish (1731—1810) was a more rigid investigator, who, having discovered hydrogen by the action of sulphuric or hydrochloric acid on iron or zinc, proceeded to examine exhaustively the properties of this new gas. He noted that like weights of metal gave him the same volumes, but that different weights of metals gave him different volumes of the gas. He concluded that hydrogen was either phlogiston or a combination of phlogiston with water, and that dephlogisticated air (oxygen) when combined with phlogiston (hydrogen) produces water.

He discovered the solubility of carbonates of the alkaline earths in excess of carbonic acid water, and discovered nitric acid. He was thoroughly saturated with the phlogistic theory, and all the useful deductions which his careful methods would have given him were thrown away by the distortions of the obvious bearing of his experiments which the phlogistic theory necessitated. When Lavoisier had triumphantly overthrown this dragon, Cavendish abandoned chemistry, simply remarking that it was hard to determine which of the rival theories was true.

Passing over the labours of the phlogistonists, Scheele, who discovered chlorine and fluo-silicic acid, and who believed light and heat to be fire and air; the first with more and the second with less phlogiston; and Bergmann, who systematised wet analysis, proved the existence of carbonic acid in the air, and introduced dry qualitative blowpipe analysis; we come to the first of a number of great figures in the history of modern chemical theory whose mission it was to open the door of the exact science of to-day and to indicate the route of those who followed him.

Lavoisier (1743—1794). His first chemical work was the experimental proof that water did not become an earth by boiling, but that the residue observed by boiling in a glass vessel was derived from the glass. His own discoveries are meagre in comparison with those of many of his contemporaries; but he greedily absorbed all that was discovered by others and changed it from crude and disconnected facts into an harmonious and consistent system.

All of his contributions to chemical science were of this character, even that great conception of the difference between the least distinguishable part of a certain kind of matter, and the least part which can take part in chemical reactions—the germ of the future distinction of the then unknown atom and molecule.

The last entrenchment of the phlogistonites was in the observed action of acids on certain metals whereby hydrogen (phlogiston) was produced. "If," they said, "a metal be not a combination of a calx with phlogiston, whence comes the phlogiston produced by the experiment?" The obvious answer was that it came from the acid, but what part? The acid was thought to unite with the metal and dephlogisticate it. Priestley and Cavendish had shown that hydrogen (phlogiston) and dephlogisticated air combined and in great part disappear. What became of them was not satisfactorily settled for a quite surprisingly long time. The fact that a little moisture was observed in the apparatus was probably ascribed to the sudden expansion and contraction of volume of the gases, since these matters and the hygroscopicity of the air were only beginning to be understood. When, therefore, Cavendish announced his discovery of the composition of water, Lavoisier applied it to the theory of combustion with such telling effect that it once and for all overthrew and destroyed phlogiston.

But though this was a glorious service of Lavoisier, it was far from all that chemistry owes to him. The new conceptions required a new language to express them, and Lavoisier with Guyton de Morveau established a system and a nomenclature so perfect as to form the framework enclosing within itself all systems which followed.

A series of definitions and rules for naming new combinations as well as a partial list of elements were parts of this system.

Lavoisier came back to Robert Boyle's definition of an element as a body which cannot be decomposed into simpler ones. The table of these elements, published by the French colleagues, contains also heat and light, but this was not in conformity with the opinion of Lavoisier, who was far too careful a student of nature to commit himself to any such gratuitous assumption; but rather more probably a concession made to the defeated phlogistonists and a means of avoiding the necessity of explaining that about which the views of scientific men were very conflicting, and nothing was certainly known.

One generalisation Lavoisier allowed himself, and that was that all acids contain oxygen (hence the name he gave to that element). It is curious how fate punishes such generalisations whenever they are made in the infancy of our knowledge on any subject. This generalisation reflects great credit upon its proposer, and shows a rapid and profound insight into many facts, but it was not many years afterwards pronounced, and is now generally considered, a fallacy, and yet if we interpret it to mean the exhibition of acid characters such as the reddening of litmus and the effect upon the senses, Lavoisier was not entirely wrong, since these characters are inseparable from the presence of water which contains oxygen.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.
June 18th, 1891.

Prof. A. CRUM BROWN, F.R.S., President, in the Chair.

MR. F. J. BLOOMER was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour o Messrs. William P. R. Newlands, Rosa, North-West Province, India; Laurence Priestley, Forest View, Noel Street, Nottingham; Thomas Armistead Ward, Preston Road, Blackburn.

The following were elected Fellows of the Society:— Tom St. John Belbin; Edward Brown; Ernest A. Congdon, Ph.B.; W. Porter Dreaper; William Duncan; Alfred John Gregory; Frederick R. Holloman; John Knowles; Frank H. Leeds; Robert Andrew Scott Macfie; Arthur Michael; Thomas Mitchell; Harry Joseph Marston Mousley; James Lane Notter, M.D.; F. M. Perkin; Edward Rhodes; Edmund Charles Rossiter; John Shields; Frank O. Solomon; John Taylor; Frederick Tetley; Dr. Otto Carl Weber; Seward W. Williams.

The following papers were read:—

29. "*A Note on Some Interactions of Dehydracetic Acid.*" By J. NORMAN COLLIE, Ph.D., F.R.S.E., University College, London.

During the last six months the author has been working with large quantities of dehydracetic acid, and he finds that several important reactions of this interesting substance have hitherto escaped notice.

In its preparation, by passing ethylic acetoacetate through a red-hot tube, it is stated that alcohol is formed; the author finds that large quantities of ethylene gas and acetone are produced as well. He also finds that dehydracetic acid is volatile to a considerable extent with steam, and is also decomposed by boiling with water to a small extent into carbon dioxide and dimethylpyrone—

$$C_8H_8O_4 + H_2O = C_7H_8O_2 + CO_2 + H_2O.$$
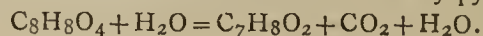
In the evaporation, therefore, of a solution of the acid,

a large quantity of the acid is lost. This decomposition into dimethylpyrone is effected far more readily if the acid is boiled with strong chlorhydric acid; if 50 grms. are boiled with the ordinary fuming acid, in about half an hour the whole is converted into carbon dioxide and a soluble compound of dimethylpyrone with hydrogen chloride. This hydrochloride crystallises from strong solutions in magnificent groups of tabular crystals. Feist states (*Annalen*, cclvii., 253) that chlorhydric acid is almost without action on dehydracetic acid.

The barium salt of dehydracetic acid seems to be not a salt of the compound $C_8H_8O_4$, but of the true tetracetic acid, $C_8H_{10}O_5$, and has the formula $(C_8H_9O_5)_2Ba$.

A curious copper salt has been obtained. If dehydracetic acid be added to a solution of copper acetate in a large excess of ammonia, on allowing to stand a pink insoluble salt separates. This salt is very stable, and is not decomposed even when boiled with sulphuretted hydrogen; but if chlorhydric acid is added it is at once decomposed and dehydracetic acid is re-formed.

The formula of the salt seems to be $C_{24}H_{25}O_9N_3Cu$. Such a salt could be produced according to the following equation :—

$$3C_8H_8O_4 + 3NH_3 + Cu(C_2H_3O_2) = C_{24}H_{25}O_9N_3Cu + \\ + 3H_2O + 2C_2H_4O_2.$$
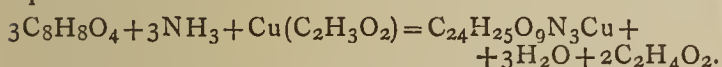
30. "*The Lactone of Triacetic Acid.*" By J. NORMAN COLLIE, Ph.D., F.R.S.E., University College, London.

In a paper which the author communicated to this Society some short time ago (*Trans. Chem. Soc.*, 1890, 189) on the constitution of dehydracetic acid, he pointed out that if the formula which he proposed for dehydracetic acid were the correct one, it would then be the δ-*lactone of tetracetic acid*. The following list was then given, which was intended to show the connection between the condensed acids formed from acetic acid :—

$CH_3 \cdot CO \cdot CH_2 \cdot CO \cdot CH_2 \cdot CO \cdot CH_2 \cdot COOH$, tetracetic acid.
$CH_3 \cdot CO \cdot CH_2 \cdot CO \cdot CH_2 \cdot COOH$, triacetic acid.
$CH_3 \cdot CO \cdot CH_2 \cdot COOH$, diacetic acid.
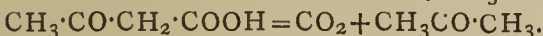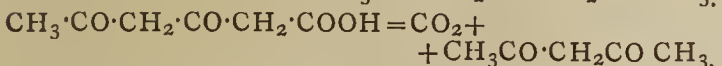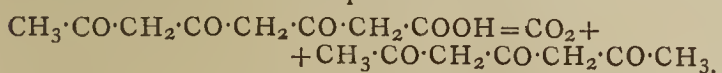$CH_3 \cdot COOH$, acetic acid.

At that time no acid corresponding to triacetic acid was known. Since then the author has, however, been able to obtain the lactone of this acid by the action of 90 per cent sulphuric acid on dehydracetic acid at a temperature of 130—135° C. :—

$$C_8H_8O_4 + H_2O = C_6H_6O_3 + C_2H_4O_2.$$
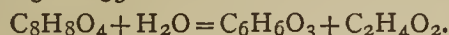
It crystallises from water in fine needles, m. p. 183° to 189° (corr.).

The properties of this new lactone resemble those of dehydracetic acid. It does not form a stable ammonium salt, for, on evaporation of a solution of the acid in ammonia over sulphuric acid *in vacuo*, a certain quantity of the acid results.

When boiled with acids or water it yields carbon dioxide and acetyl acetone, resembling dehydracetic acid and diacetic acid in this respect :—

$$CH_3 \cdot CO \cdot CH_2 \cdot CO \cdot CH_2 \cdot CO \cdot CH_2 \cdot COOH = CO_2 + \\ + CH_3 \cdot CO \cdot CH_2 \cdot CO \cdot CH_2 \cdot CO \cdot CH_3.$$
$$CH_3 \cdot CO \cdot CH_2 \cdot CO \cdot CH_2 \cdot COOH = CO_2 + \\ + CH_3CO \cdot CH_2CO \ CH_3.$$
$$CH_3 \cdot CO \cdot CH_2 \cdot COOH = CO_2 + CH_3CO \cdot CH_3.$$

When warmed with strong solution of caustic soda, acetone and acetic acid are produced.

With bromine a mono-substituted bromine derivative is formed (m. p. 200—205°) :—

$$C_6H_6O_3 + Br_2 = C_6H_5BrO_3 + HBr.$$
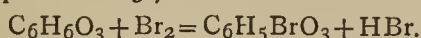
If treated with hydroxylamine an hydroxime is formed, crystallising in long needles (m. p. 230—231° (corr.).

And finally, if the ammonium salt is heated a nitrogen compound is produced, which is either a pyridine or pyrrol derivative, as it does not give any ammonia when heated with caustic soda :—

$$C_6H_6O_3 + NH_3 = C_6H_7NO_2 + H_2O.$$
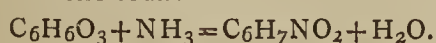
The investigation of this new compound is not yet completed.

31. "*The Refractive Power of Certain Organic Compounds at Different Temperatures.*" By W. H. PERKIN, Ph.D., F.R.S.

Having found that the magnetic relations of substances, when examined at temperatures wide apart, showed that certain variations took place after allowing for change of density, experiments having been made by the authors in reference to the refractive power of liquids under similar circumstances. After describing the apparatus used, results are given showing that the specific refractive energy of the substances examined is not constant for all temperatures. The experiments were made at temperatures from about 14 to 92, and for the lines A, C, D, and F, the differences obtained were calculated for a variation of 100°, so that comparison could be more easily made, and are as follows :—

	$\dfrac{\mu_A - 1}{d}$.	$\dfrac{\mu_A - 1}{d}p.$
Aniline	0·00310	0·2897
Toluene	0·00329	0·2910
Heptane	0·00291	0·2914
Dimethylaniline ...	0·00253	0·3057
Phenyliodide	0·00214	0·4378
Octyliodide	0·00190	0·4549
Cinnamic ether	0·00324	0·7080
Methylene iodide ...	0·00401	0·8685

By comparing the lines A and F it was also found that the dispersion was slightly diminished by rise of temperature. When calculated by Lorentz's formula, the numbers gave higher results for high temperatures than for lower ones, showing the formula is not suitable for the calculation of experiments made at high temperatures. Ketteler's experiments with water, alcohol, and carbon disulphide are also referred to. The influence of heat, therefore, affects both the refractive power as well as the magnetic rotatory power of substances ; the results, however, are not comparable as to the extent of change.

DISCUSSION.

Dr. GLADSTONE remarked that in the original paper by Mr. Dale and himself, published in 1863, they had, as the result of an examination of twenty-three different liquids, come to the conclusion that—

$$\frac{\mu - 1}{d}$$

was "nearly a constant" at all temperatures. They had tested this for the theoretical limit of the spectrum according to Cauchy's formula, as well as for the lines A and H. Landolt and Wüllner seem to have expected that the slight differences recorded were due to experimental error, but on carefully repeating the experiments they arrived at a similar result. Dufet, in 1885, published an elaborate paper, in which he proved that the general law was not absolutely true, but a near approximation. Nasini and Bernheimer, in 1884, published very careful observations both on saturated and unsaturated compounds, dealing both with the specific refraction and dispersion ; while Weegman and others have also contributed material to the general investigation of the subject.

Dr. Perkin's experiments were particularly valuable on account of the indications they give that the rate of change of specific refraction is greater at high than at low temperatures, and as they afforded clearer proof than has been hitherto given that the specific dispersion does increase with the temperature. If it should be found to be a general fact that the change is proportionally greater in saturated than in unsaturated compounds, and still greater in such bodies as cinnamic ether, another connection will have been established between this phenomenon and what we already know of refraction, dispersion, and magnetic rotation.

The observation that the values decrease as the temperature rises if calculated by the old formula, while they

increase as calculated from Lorentz's formula, seemed to be an argument in favour of the older formula; as the hotter liquid is approaching the condition of a gas, and it is well known that the refraction of a substance is somewhat smaller in the gaseous than in the liquid state.

Professor THORPE said that it would be specially important to study the influence of temperature on refractive power in the case of liquids, such as acetic acid, which were believed to undergo molecular change; and it would also be interesting to know what was the behaviour of the phosphorus compounds, as the optical properties of many of these were most anomalous.

Mr. HIBBERT thought that the superiority of the—

$$\frac{\mu - 1}{d}$$

formula over Lorentz's formula brought out by Dr. Perkin was an important result.

32. "*Note on a Volatile Compound of Iron and Carbonic Oxide.*" By LUDWIG MOND, F.R.S., and F. QUINCKE, Ph.D.

The authors describe experiments from which they conclude that iron forms a volatile compound with carbonic oxide of the formula $Fe(CO)_4$ corresponding to that of nickel. Very finely divided iron—obtained by reducing iron oxalate by hydrogen at a temperature but little exceeding 400°, and allowing it to cool to 80° in hydrogen—when heated in an atmosphere of carbonic oxide, gave a gas which burnt with a yellow flame; and on passing the gas through a heated tube, a mirror of iron was formed at between 200° and 350°, while at higher temperatures black flakes of iron and carbon were deposited. Only about 2 grms. of iron, however, was volatilised after six weeks' treatment of 12 grms. of the metal; it was necessary every five or six hours to interrupt the operation and to re-heat the iron to 400° in hydrogen during about twenty minutes. When passing carbonic oxide at the rate of about 2½ litres per hour, not more than 0·01 grm. of iron was volatilised, corresponding to less than 2 c.c. of the compound $Fe(CO)_4$ in a litre of gas. The authors have effected an analysis of the compound by passing the mixture of gases into mineral oil boiling between 250° and 300°, and heating the solution so obtained to 180°; iron free from carbon is then deposited, and carbonic oxide gas is evolved. Five analyses are quoted, the results of which give a ratio of Fe : CO, varying only from 1 : 4·03 to 1 : 4·264.

DISCUSSION.

Dr. ARMSTRONG said that the authors' discovery was even more interesting than that of the nickel compound which they had previously described in conjunction with Dr. Langer, on account of the explanation which it might be held to afford of the permeability of iron by carbonic oxide at high temperatures, as well as of the production of steel by the cementation process, phenomena t which Graham had drawn attention. Just as platinum was permeable by hydrogen and silver by oxygen at high temperatures, so iron was permeable by carbonic oxide : it might be supposed in each case, because a dissociable compound of the metal with the gas was formed.

Professor THORPE, after referring to the value of authors' observation as shedding light on the production of steel by the cementation process, stated that in studying, in conjunction with Mr. Ellis, the interaction of nitrogen peroxide and carbonic oxide under the influence of finely divided platinum, he had recently had occasion to observe that platinum had the property of causing the separation of carbon from carbonic oxide.

Mr. MOND, in reply, said that, although the application of their discovery in the directions indicated had not escaped their notice, they had refrained from discussing such matters, as the compound was only obtained at low temperatures.

Dr. ARMSTRONG said that this might well be the case; but, as Mr. Mond and Dr. Quincke had established the all-important fact that iron had a specific affinity for carbonic oxide, the argument he had used would apply, although the compound might not be sufficiently stable at high temperatures to exist alone.

33. "*The Formation of Salts—a Contribution to the Theory of Electrolysis, and of the Nature of Chemical Change in the Case of non-Electrolytes.*" By HENRY E. ARMSTRONG.

The author draws attention to the recent researches of Claisen, W. Wislicenus, and others, which clearly show that ethereal salts, such as ethylic acetate, form compounds with sodium ethylate, and to the bearing which these results have on the theory of the formation of salts generally. It may be supposed that in all cases the acid and the "base" in the first instant combine, and that the salt is formed by subsequent interactions within the molecule. In like manner, acids form dissociable compounds with water, and it is by the occurrence of change within such systems under the influence of an electromotive force that electrolysis is effected.

In those cases in which the compound is highly unstable and prone to dissociate, the opportunity for change to take place within the system is but slight, and consequently the acid is a weak one, and its solution of relatively low conducting power. In the case of non-electrolytes the occurrence of change may, in like manner, be supposed to occur within complex systems formed by the union of the interacting substances—systems which are comparable with those formed by the union of acid and "base."

34. "*Dibenzyl Ketone.*" By SYDNEY YOUNG, D.Sc., Professor of Chemistry, University College, Bristol.

Dibenzyl ketone was prepared by Popow (*Ber.*, vi., 560), by the action of heat on calcium phenylacetate.

The author finds that when the calcium salt, dried at 130°, is heated in a hard glass tube in a combustion furnace, the yield is very poor, even when the temperature is kept as low as possible, and when a current of dry carbon dioxide is passed through the tube. After laborious purification of the product, not more than 27 per cent of the theoretical amount of pure ketone was obtained.

The action of heat on the calcium salt was then more carefully studied, and it was found that the decomposition begins at about 360°, and is very rapid at 445°, the boiling-point of sulphur.

A considerable quantity of calcium phenylacetate was then heated by means of the vapour of boiling sulphur in a special apparatus described fully in the paper. More than 50 per cent of the theoretical was obtained by crystallisation of the crude product from small quantities of ether, and by fractionation and subsequent re-crystallisations of the residues, the total yield of pure ketone was increased to 76·6 per cent.

Pure dibenzyl ketone melts at 33·0°, and boils at 330·55° under normal pressure.

35. "*The Vapour Pressures of Dibenzyl Ketone.*" By SYDNEY YOUNG, D.Sc., Professor of Chemistry, University College, Bristol.

Constant temperatures above 280°, the boiling-point of bromo-naphthalene, may be obtained by means of the vapour of mercury boiling under known pressure, but there are serious objections to this substance. Benzophenone gives very good results according to Crafts (*Amer. Jour. Sci.*, v., No. 5), but the boiling-point, 306°, is not sufficiently far removed from that of bromonaphthalene to give a good range of temperature. Dibenzyl ketone boils at 330·55°, and although it suffers a slight amount of decomposition on long continued boiling, the temperature of the vapour is not perceptibly effected. The ketone may also be readily purified by re-crystallisation from small quantities of ether.

The vapour pressures from 230—280° were determined in a modified distillation bulb, the temperature being measured with a mercurial thermometer standardised by means of bromonaphthalene. At higher temperatures a

mercury vapour pressure thermometer was employed, and the ketone was boiled in a wide glass tube, enlarged into a bulb at its lower end.

Four series of determinations were made with very concordant results.

The logarithms of the pressure were mapped against the temperature, and the constants for Biot's formula (log $p = a + bat$), were calculated from the values at 230°, 280°, and 330°.

From these constants the vapour pressures were calculated at each 10° from 230—330°, and for each degree from 280—330°.

The results are tabulated in the paper.

36. "*The Vapour Pressures of Mercury.*" By SYDNEY YOUNG, D.Sc., Professor of Chemistry, University College, Bristol.

In vol. xlix., p. 37—50, of the *Trans.*, an account was given by Dr. Ramsay and the author of determinations of the vapour pressures of mercury at several widely different temperatures, and tables of vapour pressure, based on these results, were added. The highest temperature at which observations were made was that of the vapour of sulphur boiling under atmospheric pressure, and in calculating the results the boiling-point of sulphur given by Regnault was taken as correct.

From a recent research by Callendar and Griffiths (*Phil. Trans.*, clxxxii., A, 119), it appears, however, that Regnault over estimated this temperature by nearly 4°, and the vapour pressures of mercury at high temperatures therefore require correction.

Messrs. Callendar and Griffiths have also re-determined the boiling-point of mercury by means of their platinum thermometer, and the temperature they have observed is about 1·5° lower than that given in the tables of Ramsay and Young.

Two additional observations of the vapour pressures of mercury at 183·75° and 236·9° have been made, and from the previous results by Ramsay and Young (corrected at the highest temperature for the alteration in the boiling-point of sulphur), the boiling-point of mercury given by Callendar and Griffiths, and the values at 183·75° and 236·9°, the vapour pressures of mercury at each 10° from 180—480°, and for each degree from 330—360° have been re-calculated, and the tabulated results, with an account of the method of calculation, are given in the paper.

Extraordinary General Meeting, June 25th, 1891.

Prof. CRUM-BROWN, President, in the Chair.

The request of certain Fellows to the President to summon an Extraordinary General Meeting of the Society and the notice convening the meeting were read, and on the motion of the PRESIDENT it was agreed that the proposals submitted for amending and altering the bye-laws should be taken as read, printed copies having been circulated among the Fellows.

The PRESIDENT suggested that the most convenient course would be for the Fellows at whose request the meeting had been called to explain and justify in general terms their proposals, and to leave the discussion of details to a later period. Mr. JAMES WILSON, however, urged that as specific resolutions had been submitted, the several bye-laws should be separately considered, and the President having agreed that this course would be in accordance with his ruling if the motion were confined in each case to an affirmation of the principle, Mr. WILSON moved :—
" That Bye-law I. be altered in the sense indicated by the clauses already in the hands of the Fellows." He then indicated, with special reference to Clause 3, the reasons which, in the opinion of the memorialists, rendered such alterations desirable.

The motion was seconded by Dr. TEED.

Prof. TILDEN, in his capacity as President of the Institute of Chemistry, strongly deprecated the proposal that Fellowship of the Chemical Society should be regarded as a professional qualification.

Mr. CARTEIGHE then moved the following amendment :
" That this meeting declines to pledge itself to any amendment or modification of the bye-laws which has not been approved and recommended to the Fellows for adoption by the Council."

Sir F. A. ABEL seconded the amendment.

Mr. CASSAL, Mr. LLOYD, and Dr. NEWTON addressed the meeting in support of the original motion. Mr. WARINGTON, Mr. PAGE, Dr. ODLING, and Mr. FRISWELL spoke in favour of the amendment.

Mr. CLAYTON spoke in answer to objections made by Mr. Page to the use of the letters F.C.S., &c., under certain circumstances.

Mr. GOFFIN also spoke.

Mr. Lloyd and Dr. Teed having been nominated tellers for the original motion, and Messrs. Groves and Warington for the amendment, the meeting then divided. The votes recorded were—

For the amendment	137
Against ,, ...	47
Majority for the amendment ..	90

Prof. ODLING then took the Chair, and declared the following resolution carried :—
" That this meeting declines to pledge itself to any amendment or modification of the bye-laws which has not been approved and recommended to the Fellows for adoption by the Council."

On the proposal of Dr. TEED, seconded by Mr. CARTEIGHE, a vote of thanks to the President for his conduct in the Chair was carried.

PHYSICAL SOCIETY.
June 26th, 1891.

Prof. W. E. AYRTON, F.R.S., President, in the chair.

OWING to an examination being conducted in the Physical Laboratory of the Royal College of Science, the meeting was held in the Central Institution of the City and Guilds of London Institute.

Mr. J. ENRIGHT, B.Sc., was elected a member of the Society.

The following communications were made :—

"*The Construction of Non-inductive Resistances.*" By Prof. W. E. AYRTON, F.R.S., and Mr. T. MATHER.

In making some transformer tests, about three years ago, the authors had occasion to consider the construction of electric conductors the impedances of which should be practically equal to their resistances. This condition could only be fulfilled by making the inductance small in comparison with the resistance, and, as the former does not depend on the material employed (excepting iron), it was important to use substances of high specific resistance. Carbon or platinoid being available, the latter was chosen on account of its low temperature coefficient. One form of resistance exhibited consisted of strips of thin sheet platinoid, about 6 m. long and 4 c.m. wide. Each was bent at the middle and doubled back on itself, thin silk being placed between the contiguous parts and narrow ribbon used to bind the parts together. Twelve such strips arranged in series had a resistance of 2·95 ohms, and would carry a current of 15 ampères without changing its resistance more than one-tenth per cent. This strip resistance was made by Messrs. C. G. Lamb and E. W. Smith, who at that time (1888) were students in the Central Institution, and to whom the authors' best thanks are due for the praiseworthy manner in which they surmounted the difficulties which presented themselves. Another form of resistance, designed for

portability, consisted of bare-wire spirals, each length having a left-handed spiral placed within a right-handed one of slightly larger diameter, and the two being connected in parallel. This device was found to reduce the inductance to one-tenth or one-twentieth of that of a single spiral, according as the diameters of the spirals approach towards equality. When the spirals are made of platinoid wire the ratio of inductance to resistance is very small, averaging about 1-500,000th.

"*On the Influence of Surface Loading on the Flexure of Beams.*" By Prof. C. A. CARUS-WILSON.

Referring to the practical treatment of problems on beam flexure as based on Bernouilli's hypothesis that the bending moment is proportional to the curvature, the author pointed out that this assumes that the cross sections remain plane after flexure, and neglects the surface loading effect. The present paper describes experiments made to determine the actual state of strain in a beam doubly supported and carrying a single load at the centre, the effect of surface loading being taken into account. The method of investigation assumes that—

(1) The true state of strain at the centre of a beam may be found by superposing on the state of strain due to bending only that due to surface loading without bending.

(2) The state of strain due to surface loading only may be found, with close approximation to truth, by resting the beam on a flat plane instead of on two supports.

(3) The strain due to bending alone may be obtained from the Bernouilli-Saint-Venant results.

Before proceeding to describe the experiments, a short account of the mathematical work previously done on the subject was given. The nearest approach to the particular case here dealt with had been worked out by Prof. Bouissinesq, who has shown that, for an infinite elastic solid bounded on one side by a plane surface and loaded along a line on that surface, the stress (y) on an element on the normal through the middle point of the line varies inversely as its distance (x) from the surface. The formula thus arrived at was—

$$y = 0.64 \frac{P}{x},$$

whilst for a finite beam, centrally loaded, the author's experiments gave—

$$y = 0.726 \frac{P}{x}.$$

The experiments were made on glass beams mounted in a steel straining-frame, and placed between the crossed Nicols of a polariscope. Steel rollers, 2 m.m. in diameter, served as supports, and the central load was applied by a screw acting on a roller of similar diameter. Deflections of the beam were measured by a micrometer screw, at a point opposite the central load, and traversing screws enabled the whole frame to be moved so as to bring any portion of the beam in the field of view. Circularly polarised light was sometimes used, and a micrometer eyepiece served to measure the distances between interference fringes produced by loading. By carefully chosen experiments the author had shown that if a beam of glass be laid on a flat surface, and loaded across its upper surface, the shear at any point on the normal at the point of contact of the load is inversely proportional to the distance from the point of contact. In the first experiment the crossed Nicols were set at 45° to the axis of the loaded bar; a quarter-wave plate was then placed between bar and the analyser, and the position of the black spot at the point where the effect of the shear on the polarised light was equal, and opposite to that produced by the quarter-wave plate, was noted. A second quarter-wave plate was then superposed on the first; the black spot moved upwards to a point where the shear was double that at the first position. This position having been determined, one quarter-wave plate was removed, and the load diminished until the original spot moved up to the second position, and the processes repeated.

By this means a series of positions, at which the shears were in the proportions 1, 2, 4, 8, &c., were determined. Plotting the results showed the curve connecting the shear and the distance from the point of contact to be hyperbolic. Other experiments showed that the shear at any point was proportional to the load. By maintaining a constant load and measuring the distances between the interference fringes below the point of contact the hyperbolic law was confirmed.

The effect of bending a beam is, according to hypothesis, to put the upper portion in longitudinal compression, and the shear (vertical stretch) varies as the distance from the centre of the beam; the shear due to surface loading is a vertical squeeze, and, as shown above, varies hyperbolically. When, therefore, the beam is subjected to both actions, the straight line representing the bending strain may intersect the hyperbola representing the shear due to surface loading in two points, and, since at the corresponding points in the central section the shears are equal and opposite, the elements are only subjected to voluminal compression, and will exert no birefringent action. Hence, when viewed through crossed Nicols, black spots will be seen on a white field. Keeping the load constant and diminishing the span should cause the spots to approach each other, and when the line is tangential to the hyperbola the spots coincide. These deductions were confirmed by experiment, and it was found that, for a span of less than four depths, no point of zero shear exists on the central section. The strains in beams subjected to surface loading were thus shown to be of a character different from those usually assumed, the neutral axis, instead of coinciding with the axis of the beam, being lifted up in the centre, and its shape depending on the load and span.

Other ingenious and interesting experiments on beams were described, in some of which the lines of principal stress were mapped out. Remarkable results were obtained, showing that, although the tension lines given by Rankine and Airy are nearly correct, the curves of compression may be very different and have very curious shapes.

Prof. PERRY thought the local loading effect would not be so important in long beams, and inquired whether, in ordinary test-pieces, local loading would affect the breaking strength. He also asked what effect the fact of the load making contact over a surface, instead of along a line, would have on the results; and in reply Prof. CARUS-WILSON said the effect was to raise the asymptote of the hyperbola, representing the surface loading stress, above the surface of the beam.

On "*Pocket Electrometers.*" By C. V. BOYS, F.R.S.

This communication described modifications of electrometers adapted for portability. As quartz fibres increase the delicacy and diminish the disturbing influences affecting instruments, much smaller controlling forces can be employed than when silk is used for suspensions. He had, he said, pointed out some time ago the great advantages arising from making galvanometers small. Applying similar reasoning to electrometers, he remarked that making an instrument one-tenth the size of an existing one reduced the moment of inertia of the needle to $\frac{1}{10^5}$—whilst the deflecting couple for given potentials would only be one-tenth of its former value. The small instrument would, for the same periodic time, be 10,000 times more sensitive than the large one, provided the disturbing influences could be reduced in the same proportion. This, however, was not ordinarily possible, for any method of making contact with the needle—such as by a fine wire dipping into acid or mercury—prevented very small controlling forces being used. Still, by suitable devices, a large proportion of the full advantage could be obtained; a freely suspended needle without liquid contact was essential to success. The first instrument described was one in which the needle was cylindrical, contiguous quarters being insulated and connected to the opposite

ends of a minute dry pile placed within the needle; opposite quarters were then at the same potential, and at a different potential to the other pair of quarter cylinders. This was suspended within a glass tube silvered on the inside, and divided into four parts by fine longitudinal lines. In such an instrument the needle and quadrants are reciprocal, and the deflection depends on the product of the difference of potential between the quadrants and that between the parts of the needle. Owing to the dry pile not being constant the instrument was found unreliable, but when working at its best a Grove cell would give 30 or 40 m.m. deflection. The next step was to make a cross-shaped needle of zinc and platinum, and rely on contact electricity to keep the parts of the needle at different potentials. This bold experiment proved remarkably successful, for the instrument was very sensitive. A disc-shaped needle, with quadrants alternately zinc and platinum, was then employed, and by this a small fraction of a volt could be measured. The weight of the disc was only 1-20th of a gramme, and the instrument could be turned upside down or carried about in the pocket with impunity. Another small instrument, with the stationary quadrants of zinc and copper, was exhibited, and by rotating them through an angle of 90°, so as to bring them in a different position relative to the parts of the needle, a deflection of several degrees of arc was produced.

In the course of his remarks Mr. Boys made several suggestions relating to Ballistic Electrometers and Electrostatic Siemens' Dynamometers, and pointed out the possibility of instruments, such as he had exhibited, being of use in elucidating the obscure points in connection with so-called "contact electricity."

The PRESIDENT complimented Mr. Boys on the beautifully simple and remarkably sensitive electrometers exhibited. He remembered that some years ago Mr. Gordon made a very small electrometer, but its insulation was insufficient for electrostatic work. He agreed with Mr. Boys as to the advantages of small instruments, providing sparking across or tilting of the needle could be prevented. On the other hand, he thought the use of small potential differences on the needle was a step in the wrong direction, when great sensibility was required.

Prof. PERRY asked if the needle could not be kept charged by occasional contacts with a charged acid cup.

Mr. BOYS said he had originally intended using a fairly highly-charged needle, but had not yet done so. He also suggested that an electrometer of very small capacity might be made by reducing the quadrants surrounding a disc needle until they became like small tuning-forks.

A paper on "Electrification due to the Contact of Gases with Liquids," by Mr. J. Enright, B.Sc., and one on "The Expansion of Chlorine by Heat," by Dr. Arthur Richardson, were taken as read.

The following correction should be made in the report of the meeting on June 12th:—For the first sentence in Mr. Blakesley's remarks on Dr. Lodge's experiments, substitute—

Mr. BLAKESLEY asked whether the pitch of the resonant jars altered when the distance between the circuits was varied, for according to theory the mutual induction should diminish the self-induction and cause the oscillations to be more rapid.

The Action of Nitric Acid at Different Strengths and Temperatures upon Iron.—Henri Gautier and G. Charpy.—Nitric acid attacks iron at every degree of concentration, but the action may take place in two different manners, the one rapid and attended with an escape of gas, and the other slow and without a production of gas. The existence of these two modes of action explains very simply the phenomenon known as the *passivity of iron*, which corresponds not, as it has been hitherto supposed, to the absence of all action, but merely to a slow action without the liberation of gas.—*Comptes Rendus*, cxii., 25.

NOTICES OF BOOKS.

Photography Annual. A Compendium of Information upon Photographic Matters, and the Annals of Photography for the Past Year. 1891. Edited by HENRY STURMEY, F.S.Sc. London: Iliffe and Son.

THE number of persons who occupy themselves more or less seriously with photography is something altogether exceptional. In the windows of the opticians, cameras and their accessories seem to have displaced all other kinds of apparatus. Photographic societies have sprung up even in country towns where the talk of the natives has hitherto been almost exclusively of bullocks. Scientific societies, Young Men's Christian Associations, and even one or two "Literary and Scientific" organisations, have their photographic sections. We can only hope that Science will be benefitted by this devotion to an art which links itself in many ways not merely with chemistry and physics, but with astronomy and biology.

The goodly volume before us is not confined to matters which interest the average taker of portraits, but comprises much valuable matter on actinometry and photometry; on that grand vision of the future, photography in colours; on spectrum photography; and on astronomical photography, accompanied by a number of fine prints of the moon in different phases. But we do not find any special record of progress in the application of photography to micro-biological investigation.

We notice a very appropriate utterance of one of the contributors, *viz.*, that it "is not the true function of any art process to ape the productions of any other process." We must not regard it as high praise if we are told that "a photograph looks more like a sepia drawing than a photograph."

An essay on photographing animals is spoiled by the introduction of a phrase which is one of our most unfortunate "insular peculiarities." The writer, though a F.Z.S., speaks of the love or fear men bear towards the *dumb* creatures around them.

The paper on "Naturalistic Photography" is followed by its antidote in the shape of "Musing on some Recent Mistakes." The writer is justly severe on a school of artists, whether with camera or brush, who "cannot represent a girl feeding a dove, or picking a bunch of grapes, without giving her an expression of unutterable woe."

A paper headed "My Lantern" is a severe critique on dissolving views in any shape or form. They may do, he thinks, for "Sunday-school meetings, tea-fights, or for Temperance lectures." But, *minus* of course the dissolving, camera views are the best means of illustrating scientific or educational lectures. How poor, in comparison, is the "drawing lecture," where a sensational speaker strives to reproduce some animal or vegetable structure by dint of a black board and a piece of chalk!

The advertisements, introduced in the American manner among the text, are so numerous that the would-be purchaser is puzzled no less than the would-be reader.

Of the illustrations some are beautiful. But we are sorry to meet with our old enemy, "Portrait of a Lady," which, with the accompanying bore, "Portrait of a Gentleman," make the Royal Academy Exhibitions to many persons anything but "a joy for ever."

"Goring Church" makes as near an approach to the effect of reflections in a river as can be hoped for in case of water which is not absolutely at rest. The "Night-blowing Cereus" is a novelty; the plant is cheated into being taken by the instantaneous process. The "Silver-cup Picture" is probably suffering from face-ache. The "High Tor, Matlock," would have been more pleasing if the scenery had not been suffering from an infliction of snow.

"Miss Elsie" is a clever likeness, but the damsel herself seems to be in a winterly frame of mind.

The illustration of the collotype " In the West Indies " is excellent in its execution, but it would have been easy to find in most of the Antilles a more fascinating landscape.

To find a book of a thousand closely printed pages offered at such a low price is indeed a sign of the times, and is a fresh proof of the widespread interest taken in photography.

The Pocket-book of Mensuration and Gauging, &c ; for Revenue Officers, Brewers, Spirit Merchants, &c. By J. B. MANT, Inland Revenue. Second Edition, revised. London: Crosby Lockwood and Son.

THE author, in his Preface, announces that he has intended to furnish not a text-book, but an aid to memory when bulkier works for reference are not at hand.

This Pocket-book, from its intensely technical nature, is scantily intelligible to persons who have neither been trained for the Inland Revenue service, nor brought up to brewing, distillery, and the sale of excisable liquors. It contains an account of logarithms; of the slide-rule; method of alligation; a description of the hydrometer and saccharometer used by the Revenue; rules for blending, mixing, and reducing spirits; the chemical formulæ of the distillers' raw materials and products; instructions for finding the area of certain figures; the mensuration of solids. Then follow instructions for gauging stills; ullaging; directions—rather rough—for taking the specific gravity of a solid; beer gravity tables; beer duty calculator; tables of weights and measures, both English and metric; original gravity tables. Lastly come particulars of excise licences.

How do I Stand ? being Hints and Directions in Book-keeping and Balancing for Retail Chemists. By GEORGE WEDDELL. Newcastle-on-Tyne: Mawson, Swan, and Weddell.

THE title of this little book, as it appears on the outside, led us to suppose that we had before us a treatise on the mechanism by which man is enabled to maintain the erect attitude. On opening the book we found it to be a manual of book-keeping, specially adapted for the guidance of the pharmaceutical profession, who, if the author is to be believed, have somewhat neglected this department of their business.

In the introductory portion of the work an attempt is made to answer the question why pharmacists do not become rich in the same proportion as drapers, &c. ? To this query the writer replies, that it is " because they do not carry on their business on the same common-sense principles that others follow." Our opinion—whatever it may be worth—is that the pharmacist of necessity carries on his operations on a limited scale. People do not stroll into a pharmacist's shop to look round and see if there is anything they fancy. They buy medicines simply if they need them. Further, as far as the law allows, they are shamefully encroached upon by other tradesmen, especially by the monopolist drapers of the present day. At present any person can sell poisons, if only made up as a " patent," without any knowledge or care about their properties, without any caution given to the customer, and without any responsibility in cases of accidents.

Appendix to the Report of the Minister of Agriculture. Experimental Farms for 1890. Ottawa: Brown and Chamberlin, Queen's Printers.

THIS work comprises special reports of the director, the agriculturist, the horticulturist, the chemist, the entomologist and botanist, the poultry manager, and the superintendents of the four experimental farms.

The director makes the suggestive remark that " a large proportion of agricultural products appear to have a life-period, some short, some long, after which their vigour or vitality becomes gradually impaired until their cultivation can no longer be continued with profit." He shows that, by a delay of one week in the time of seeding, the farmers of Ontario may lose 2½ million dollars on the barley crop alone.

The fruit-growing capacity of the Dominion is not as yet sufficiently estimated in England. Even in grapes it may successfully compete with the European continent. From 400 to 500 tons of grapes were shipped last year from " small stations in the Niagara district."

Varieties of apples, pears, and plums, of Russian origin, seem to succeed well.

Attention is being wisely given to planting forest trees on the plains, where their shelter will be of the highest value, not merely to fields and orchards, but to the stockyards and the homes of the settlers. Wind is, perhaps, the greatest enemy to horticulture.

As fungicides salts of copper have proved very successful, but further experiments will be needed to decide what proportion is most deadly to fungi and least harmful to the trees themselves.

The chemist regards potash and phosphoric acid as the most important mineral constituents of a soil, and lime as the principal of " the inorganic elements of minor importance." He recognises lime (in the state of carbonate) as taking part in the process of nitrification. An excess of nitrogen, he considers, " promotes a rank growth of straw." Gypsum he finds of especial value for leguminous plants—a result which agrees with English practice.

For dressing seed-wheat, in order to destroy smut, ferrous sulphate seems much preferable to copper sulphate, as the latter was found to impair the vitality of the seeds to a serious extent, 26·5 per cent.

The Department of Agriculture offers to farmers to analyse their well-waters freely if they will pay for the carriage of samples. It appears that out of ten samples only three could be reported safe to drink.

A curious fraud has been devised for the injury of bee-keepers. " Foundation-comb " is a common article of sale beyond the Atlantic, as it saves the bees much time and labour. But the wax used for this artificial comb is largely adulterated with paraffin. As this article melts at a much lower temperature than genuine wax, in hot weather the comb breaks down ; the honey is spoiled, the young brood smothered, and the bees smeared with paraffin to their disgust and injury.

From the report of the entomologist we learn that injurious insects are a tax of 10 per cent on all farm produce. In many seasons the loss will, we fear, be much greater.

The House Surgeon, or the Doctor at Home. Containing Instructions for the Prompt Treatment of Accidents and Emergencies before the Arrival of Medical Aid. By the late ALFRED SMEE, F.R.S., Surgeon to the Bank of England. Compiled specially for the Accident Insurance Company, Limited. London: The Accident Insurance Company, Limited.

As regards the methods of treatment here advised, only the practical physician or surgeon is, in most instances, competent to form an opinion. In the instructions for the treatment of poisoning cases, two of the most formidable substances, chrome and barium, are overlooked. This is the more to be regretted since both these substances are largely used in the arts. For any soluble compound of barium, Epsom salts or sulphate of soda should be used. For chrome there is probably no remedy but the prompt use of the stomach-pump. For all cases where strong coffee is recommended, it must be remembered that the ground coffees sold in tins, under the mendacious names of " Coffee as in France " or " French Coffee," will not be of the slightest use.

The caution to policemen not to treat persons who are

in a fit, or who have been stunned, as if drunk, is very needful. The commencement of fevers and the approach of apoplexy often cause the patient to walk unsteadily.

The application of " laundresses' blue " for the stings of wasps, &c., is the more mysterious as this article has completely altered its nature. Formerly it was smalts,—a preparation of cobalt, rarely free from a trace of arsenic,—or sometimes a preparation of indigo. Now it is artificial ultramarine. It is scarcely conceivable that substances of such different chemical composition should have the same physiological action. Caustic ammonia. which is in fact recommended in an earlier part of this pamphlet, will be found preferable if the injury is not on or near the eye.

Alkali Works Regulation Act, 1881. Twenty-seventh Annual Report on Alkali, &c., Works. By the CHIEF INSPECTOR. Proceedings during the Year 1890, presented to the Local Government Board and to the Secretary for Scotland. London: Printed for Her Majesty's Stationery Office, by Eyre and Spottiswoode.

THE inspection of alkali works, or, as we may rather say, chemical works, is still carried on satisfactorily. The Chief Inspector states that the analysis of the air or gases escaping up the chimney is now recognised as an essential part of the daily duty. The total number of works under inspection is 1034, of which 133 only are alkali works strictly speaking. The amounts determined are remarkably uniform, " agreeing year after year within small fractions of a grain."

During the year 1890 there has been no prosecution for any infraction of the Act, and, what is more, no complaints have come in from farmers and others as regards damage done by noxious vapours. To this satisfactory state of things there is one only exception. The Chance process for utilising the sulphur present in the tank waste has encountered " unexpected difficulties and partial disappointment." Many modifications of the original process have been devised, and have been under certain circumstances successful. The Chief Inspector hopes that ultimately neither hydrogen sulphide nor sulphur dioxide will escape into the air.

The salt trade, as compared with 1888, has fallen off by 12 per cent, owing to the enhanced price of fuel. The total salt consumed in the United Kingdom in 1890, in the alkali manufacture has been 885,029 tons, of which 632,769 tons have been used in the Leblanc process.

The production of sulphate of ammonia has risen from 122,785 tons in 1888 to 134,257 tons in 1890. This increase would doubtless have been greater if the yield from the iron and coke works had not been interfered with by the prolonged strike in the iron trades.

Improvements have been attempted in the process for recovering the ammonia, &c., liberated in coke ovens. The admission of air, however, partly destroys the ammonia and modifies the other products. The Mond process seems to have but a doubtful future unless coal becomes cheaper and ammonia commands a higher price.

The combined alkali process of Parnell and Simpson, we are told, has not fulfilled the hopes of its promoters, and the experimental work is for the present abandoned. On the other hand, Dr. Affleck, the Widnes inspector, considers that the Haddock and Leith process has some decided advantages over the Chance, the Gossage, and the Solway processes.

It is rather a novelty to find black coal smoke referred to in the reports under the Alkali Act. It is evident that the smoke escaping from chemical works is a trifle in comparison with that generated by iron works, by locomotives on railways, and by marine engines on navigable rivers and in harbours.

As regards the smoke from dwelling-houses, Mr. Fletcher states that he has lived for five winters " in a house where no bituminous coal was burnt, and no contribution was made to the smoke of London." This is

so far very well ; but if even half the householders in London were to adopt this expedient the price of non-bituminous coal would quickly reach a prohibition point.

As regards the manufacture of cement we find a remark which is no longer applicable. The manufacture is said to have been " very brisk." It is now exceedingly slack, partly from rampant competition and partly from strikes and rumours of strikes. Some of the professional agitators think themselves entitled to interfere in the management of all chemical works, and it is now difficult to discharge a drunken or dishonest workman without the threat that the workmen will be " called out."

CORRESPONDENCE.

ON THE PRODUCTION OF MUSICAL NOTES FROM NON-MUSICAL SANDS.

To the Editor of the Chemical News.

SIR,—I have now succeeded in producing musical notes from sand that was never before musical, and am also able to produce similar results from those mute, or " killed," musical sands which have been temporarily deprived of their musical properties.

Full details will shortly be made public, but in the meantime some may be interested to know that all my experiments have been conducted on the principles involved in the theory which I propounded in 1888 to account for the emission of musical sounds from such sands, and that the results obtained appear to demonstrate indisputably the applicability of this theory. — I am, &c.,

CECIL CARUS-WILSON.
Bournemouth, June 27, 1891.

[A short time ago I had the pleasure of witnessing Mr. Carus-Wilson's experiments with musical sands—sands originally musical, musical sands which had been killed and then revived, and sands originally mute which had had the gift of music conferred on them. Mr. Wilson hopes soon to be prepared to publish his experiments and the explanation of the phenomena in detail.—W. C.]

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed

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Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxii., No. 25, June 22, 1891.

The Electrolysis of Barium Chloride, either Pure or Mixed, with Sodium Chloride.—C. Limb.—The author's experiments were undertaken with a view of obtaining metallic barium. But neither from pure barium chloride nor from the mixture of barium and sodium chlorides has he been able to obtain at the cathode even the smallest quantity of the metal. Chlorine, however, was evolved in abundance, and it appears probable that there is formed a barium or a sodium sub-chloride, or possibly a combination of both.

Calculation of the Boiling-Heat of any Liquid whatever, under any Pressure.—G. Hinrichs.—A purely mathematical paper which does not admit of useful abridgment.

Action of Heat upon the Solutions of the Salts of Chromium Sesquioxide. Green Chromium Salts.—A. Recoura.—The author concludes that within the limits of concentration in which he has been able to operate a

dissolved chromium sesquisulphate is split up completely under the influence of heat into free sulphuric acid and a soluble basic sulphate of a perfectly definite composition, $2Cr_2O_3.5SO_3$. It is derived from 2 mols. of sulphate, which lose 1 mol. of acid, and it contains a modified oxide which is unable to fix a further quantity of acid. This modified sesquioxide cannot exist in a free state, and when it is precipitated by decomposing the green sulphate with an alkali it is split up and the precipitated oxide is a new modified oxide, 1 mol. of which takes up only 2 mols. of sulphuric acid.

Researches on Osmium: Osmiamic Acid and the Osmiamates.—A. Joly.—The author has resumed the study of osmiamic acid—a compound containing both nitrogen and oxygen, discovered by Fritzsche and Struve in 1847. He prepares the potassium salt of osmiamic acid by dissolving crystalline osmium tetroxide in potassa (OsO_4 100, KOH 100, water 50). To the liquid, which is kept at 40°, he adds 40 c.c. of caustic ammonia. In a few moments the brown liquor is deposited and deposits a yellow crystalline precipitate of potassium osmiamate. When the decolouration is complete and the liquid is cold he decants, washes the salt with iced water, and dissolves it in boiling water. It crystallises on cooling in fine quadric octahedra. It is important to avoid an excess of ammonia, which would leave the potassium osmiamate mixed with a very unstable ammoniacal salt. The composition of the potassium salt is expressed by the formula $OsO_3NK + 2H_2O$. Osmiamic acid may be approximated to the nitroso-compounds of ruthenium which the author has previously described, $RuNOCl_3, RuNO(OH)_3$. If we admit the existence of a compound $OsNO(OH)_3$, osmiamic acid will be its first anhydride.

On the Alkaline Zirconates.—L. Ouvrard.—The author has obtained a lithium zirconiate by fusing lithium chloride with zirconia. He assigns to the crystallisation obtained the formula $LiOZrO_2$. Zirconium silicate behaves like an acid.

On Silicon Bromoiodides.—A. Besson.—The author has obtained and examined Si_2Br_3I—a colourless liquid which distils at 192°, and which, on refrigeration, presents a very distinct phenomenon of superfusion. The compound $Si_2Br_2I_2$ is a white solid which melts at +38°, and distils at 230—231°. The compound Si_2BrI_3 is a white solid melting at 53° and distilling at 255°. In a future paper the author will describe the preparation and the properties of boron phosphide.

On the Cyanogen Compounds of Magnesium.—Raoul Varet.—The author here describes the double magnesium-mercury iodocyanide and the corresponding bromocyanide. The action of magnesium iodide upon mercury cyanide yields a compound of magnesium cyanide and mercury iodocyanide; the action of magnesium bromide upon mercury cyanide yields a compound of the same order.

Action of Sodium Benzylate upon Campho-Carbonic Ether.—J. Minguin.—Not adapted for abstraction.

Comparative Influence of Iron Sulphate and Calcium Sulphate upon the Retention of Nitrogen in Bare Soils, and on Nitrification.—P. Pichard.—According to the author gypsum is more effective than ferrous sulphate in preventing the escape of nitrogen and in favouring nitrification.

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Moniteur Scientifique, Quesneville.
Series 4, Vol. iv., Part 2, No. 586.

Treatment of Uranium Residues.—Dr. Laube (*Zeit. Angewandte Chemie*).—The uranic residues are preserved in a large jar, the supernatant liquid being from time to time poured away until the pasty deposit containing the uranium fills about two-thirds of the vessel. It is then heated to ebullition, either by a current of steam passed into the vessel or in an iron pan over a naked fire, adding from time to time crystals of soda until the uraniferous

portion of the precipitate appears dissolved. Without filtering he pours into the liquid when cooled so much ammonia that its odour may be distinctly smelt, and then a mixture of equal parts of ammonia and magnesium sulphate, so as to throw down all the ammonium magnesium phosphate. During this last treatment the liquid must be carefully stirred. After settling for twelve hours the liquid is drawn off with a syphon, and the residue washed repeatedly with ammonia water. These liquids are passed through the filter which receives the precipitate. The alkaline liquids are placed in large vessels half-filled, and are neutralised with sulphuric or hydrochloric acid, and the carbonic acid is totally expelled by boiling. The uranium is then expelled by means of ammonia, in the form of ammonium uranate. The precipitate is easily washed at first by decantation with hot water. Afterwards it is necessary to add a small quantity of a salt of ammonium, as the precipitate otherwise would only subside imperfectly.

NOTES AND QUERIES.

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Bleaching Fat.—Will any reader kindly inform me how to bleach bone fat white?—ENQUIRER.

Separation of Cotton from Wool.—I should be glad if any of your readers could give me any information about the process for the carbonising of woollen rags containing cotton, and if there has been any book published on this subject.—G. L.

Copper Antimonide.—In the CHEM. NEWS for April 6th, 1888, (vol. lvii., No. 1488), we see a chapter on the "Occurrence in Nature of Copper Antimonide," wherein it states that there is a deposit of this mineral at Mytilene. We believe we have discovered a process that will treat this ore successfully, commercially; and our object in writing is to ask if you can by any chance put us in communication with Mr. Melcon, who is mentioned in the article as having sent over some samples of the ore.—BOWES, SCOTT, AND WESTERN.

THE CHEMICAL NEWS.

VOL. LXIV., No. 1651.

NOTES ON SOLUTIONS OF ARSENIOUS OXIDE.

By E. GODWIN CLAYTON.

THE following results of experiments made by me with arsenious oxide (As_4O_6) may be recorded, for the purpose of comparison with the results of other workers :—

Cold Aqueous Solutions.

1. Arsenious oxide shaken with distilled water (temp. 15° C.), at intervals of half an hour, for a period of four hours. Quantity dissolved, 0·118 grm. in 100 grms. of water, or 1 part in 847.

2. Arsenious oxide shaken with distilled water (temp. 15° C.), at intervals of twenty minutes, during a period of six hours. Quantity dissolved, 0·269 grm. in 100 grms. of water, or 1 in 372. Specific gravity of this solution, 1002·3. [Buchner (*J. Ph.* [3], 1, 421) gives the strength of a solution prepared from the crystallised oxide by digestion for some days at 15° C. as 0·28 per cent, or 1 in 357.]

3. Arsenious oxide shaken with water (temp. as before) at frequent intervals during four days. Quantity dissolved, 0·99 grm. in 100 grms. of water, or 1 in 101. Specific gravity of solution, 1007·9.

None of the above solutions deposited arsenious oxide when left to stand for several days.

Hot Aqueous Solutions.

4. Arsenious oxide boiled with distilled water for one hour; solution gradually cooled and allowed to rest for twenty-nine hours. Quantity of As_4O_6 dissolved, 2·23 grms. in 100 grms. of water, or 1 in 45. A duplicate experiment gave 2·22 grms. Specific gravity of solution, 1017·7. [Buchner (*op. cit.*) gives 2·18 per cent as the strength of a solution saturated at 100° C., and cooled to 15°.]

5. Arsenious oxide boiled with distilled water for four hours. Quantity found in solution in 100 c.c. of liquid, measured at about 93°, 9·52 grms., or 1 in 10½.

6. A portion of the same solution allowed to cool and stand for an hour and a half. Quantity still in solution, 8·24 grms. in 100 c.c., or 1 part in 12.

7. Another portion of the same solution left at rest for 45½ hours. Quantity remaining in solution, 3·28 grms. in 100 c.c., or 1 part in 30. Specific gravity, 1025·4.

8. Another portion allowed to stand for ninety hours. Quantity in solution, 3·21 grms. in 100 c.c., or one part in 31.

In experiments 6, 7, and 8, the separated As_4O_6 formed a crystalline film on the sides and bottom of the containing vessel, as well as a crust covering the surface of the liquid. Finely-divided crystallised As_4O_6 was used in every case. The results obtained show the large influence which the time of digestion and frequency of shaking have upon the quantity of the oxide dissolved. By prolonged digestion, with frequent agitation, it is evident that a cold aqueous solution, of considerably greater strength than that obtained by Buchner, can be prepared. The solution made in experiment 3 is seen to be of about 1 per cent strength. The solutions prepared with boiling water, and afterwards cooled and allowed to stand, as in experiments 7 and 8, were also stronger than Buchner's. In "Watts' Dictionary," First Edition, vol. i., p. 374, it is stated that a hot saturated solution, afterwards cooled, retains 1 part in 30 of the oxide—my own results corroborating this.

The minute crystals obtained on evaporating small quantities of the aqueous solutions to dryness were seen under the microscope to be, chiefly, unmodified regular octahedrons and cubo-octahedrons, together with what appeared to be triakis octahedrons and various tetrahedral forms.

Alkaline Solutions.

9. Arsenious oxide was boiled with excess of an aqueous solution of potash (1 : 10) for three hours. The quantity of oxide dissolved was estimated in 100 c.c. of the solution, measured hot, and found to be 34·08 grms., or about 1 in 3.

10. A portion of the same solution was allowed to stand for twenty-four hours. Quantity of As_4O_6 now remaining in solution, 14·29 grms. in 100 c.c., or 1 in 7. Well developed, transparent, and lustrous crystals of the oxide had been deposited in the flask.

ON THE

NATURE OF SOLUTION.

By J. ALFRED WANKLYN and W. J. COOPER.

THE solution of sugar by water affords one of the simplest and most typical examples of solution. The following facts have been ascertained by us :—A quantity of sugar in coarse powder was placed in a half-litre flask, and water poured into the flask until the half-litre mark was reached ; and the observation was made that no contraction or expansion takes place during the dissolving of the sugar.

In another experiment we weighed out 51·50 grms. of sugar, dissolved it in water in a 100 c.c. flask, filled up accurately to the mark, and weighed.

	Grms.
Weight of the 100 c.c. of sugar solution ..	119·082
Sugar..	51·50
Water	67·582

Taking the sp. gr. of sugar at 20° C. as 1·590, the volume of the sugar employed was 32·4 c.c. It is, therefore, accurately true that when sugar dissolves in water the volume of the solution is equal to the sum of the volumes of sugar and water. We attach much importance to this observation. Many far-reaching consequences flow from it. Each gramme of sugar as it enters into the 100 c.c. of solution raises the weight of the solution to the extent of 0·371 grm., and displaces 0·629 grm. of water.

The customary tables of specific gravities of solutions of different strengths are so constructed as to mask the simple relation between the strength and the specific gravity. By changing them so as to set out the specific gravities corresponding to the number of grms. of sugar in 100 c.c. of sugar solution, the regularity becomes manifest. Thus :—

No. of grms. of sugar in 100 c.c. of sugar solution.	Sp. gr.
1	1·00371
2	1·00742
3	1·01113
4	1·01484
5	1·01855
10	1·03710
20	1·07420
30	1·11130
40	1·14840
50	1·18550

The value 0·371 is the increment of specific gravity due to 1·000 grm. of sugar existing in the solution. It may be termed the increment coefficient = i.

When sugar dissolves in water there is neither rise nor fall of temperature—it is a pure and quite unmixed example of the phenomenon of solution.

Salt and Water.—We placed 73·7 grms. of salt in a half-litre flask, added water up to the half-litre mark, and made our observations. As the salt dissolved the level of the liquid fell, and when the solution was complete the contraction had become 9·0 c.c. The temperature was

almost absolutely unchanged. The specific gravity of the salt solution (containing 14·74 grms. salt in 100 c.c. of solution) was 1·0988. The increment coefficient $i = 0·670$.

The water displaced by 1 grm. of chloride of sodium is 0·330. Therefore the *liquid density* of chloride of

sodium is $\dfrac{1}{0·33} = 3·03$.

By experiment we found the specific gravity of solid chloride of sodium to be 2·13 at 17° C. The contraction which salt undergoes when it passes into solution is consequently very marked. There are two obvious ways of looking at this contraction on liquefaction—(1) it may be like the contraction when ice melts; (2) it may be due to chemical combination between the salt and the water. Which of these views is correct, or, indeed, whether both may be right and the contraction be partly the ice case and partly due to chemical combination, remains to be ascertained. Starting, however, with the liquefied salt we may ask does it behave like sugar?

Is the value i constant for all degrees of concentration? The answer returned by experiment appears to be " nearly constant but not quite constant." When the solutions are very dilute the value of i rises slightly. Thus with a solution containing 1·474 grms. salt per 100 c.c. of solution, the value of $i = 0·709$.

It is, however, to be noted that the departure from what may be called the theoretical density is very small indeed, viz. :—

Theoretical density . .. .. 1·00987
Experimental ,, ... 1·01048

Bromide of Sodium.—We have taken the specific gravity of the solid salt; we find it to be 3·20 at 16° C. When this salt dissolves in water there is a little contraction, but not so much as in the case of the chloride.

A solution of the bromide containing 50·20 grms. per 100 c.c. of solution has a specific gravity of 1·3722 at 15° C. $\therefore i = 0·741$.

A solution containing 10·04 grms. per 100 c.c. of solution had a specific gravity of 1·07606. Therefore $i = 0·757$.

In the case of the bromide i is very nearly constant for different strengths of solution.

Iodide of Sodium.—Specific gravity of solid at 16° C. we found to be 3·31. A solution containing 41·01 grms. per 100 c.c. of solution had specific gravity 1·3021 at 16° C. Therefore $i = 0·737$.

A solution containing 8·202 grms. had specific gravity 1·06128. Therefore $i = 0·747$. In this instance i is almost absolutely constant for different dilutions.

Anhydrous Chloride of Barium.—BaCl$_2$, specific gravity 3·13 (solid) dissolves in water with evolution of heat.

A solution, strength 18·372 per 100 c.c. of solution, specific gravity 1·14610, $i = 0·795$.

Anhydrous CaCl$_2$, specific gravity (solid) 1·94, $i = 0·675$.

Sulphate of Magnesia.—Specific gravity of the crystals MgOSO$_3$7H$_2$O 1·70. This case is interesting.

The specific gravity of a solution containing 62·1 grms. of crystals in 100 c.c. was 1·271.

In dissolving in water, therefore, the crystals contracted very slightly (only about $\frac{1}{25}$). If we regard the solution as a solution of anhydrous MgOSO$_3$ in water, we have the value $i = 0·890$ and 0·110 as the water displaced by

one grm. of MgOSO$_3$; and as a further consequence $\dfrac{1}{0·110}$

or 9·09 as the fluid density of MgOSO$_3$. Manifestly such a density is absurd.

It is proved, therefore, that aqueous solution of sulphate of magnesia is a solution of the crystals—not of the anhydrous salt, and the value of i for the crystals is nearly the same as i in the case of sugar.

Our view of solution is that it is simple and regular, as illustrated by sugar. It is modified by chemical changes, and its regularity is masked.

Laboratory, New Malden, Surrey.
July 13th, 1891.

RECENT INVESTIGATIONS ON THE FULMINATES.

By H. N. WARREN, Research Analyst.

THE exact nature or formulæ of fulminic acid and its compounds, owing to their extreme unstableness, even to the present time is, comparatively speaking, little known. The following experiments lately performed with these bodies, although possessed of scientific interest only, offer further contributions to our knowledge of them. On account of the extremely dangerous nature of the fulminates, necessitating the use of so small a quantity when examining them, some slight doubt naturally remains as to their exact nature. The salt used to conduct the experiments with was argentic fulminate (ordinary fulminating silver). This being dissolved in hot water and digested with copper filings was transformed into cupric fulminate; the green salt thus obtained was dissolved in water, and introduced into a tube open at either end, one extremity being closed by means of a porous diaphragm. The salt was then reduced by means of nascent hydrogen according to the usual method, namely, by connecting the same to a small Daniell's cell, the inside of the tube being provided with a platinum electrode connected with the negative end of the battery. In the course of a few hours the whole of the copper had become reduced to the metallic form, and firmly attached to the platinum plate.

The solution obtained, being thus freed from copper, was next examined, and was found to contain, besides large quantities of hydrocyanic acid and ammonia, distinct quantities of fulminic acid, evidently existing partly as the hydrogen compound and partly as ammonium fulminate. This was converted into, and further examined as, argentic fulminate by digesting the same with argentic carbonate. In every instance an explosive fulminate was re-formed, corresponding to the normal fulminate. In the next experiment cupro-ammonium fulminate was obtained by the addition of an excess of ammonia to a solution of cupric fulminate.

The deep blue crystals thus formed were, after being dried by suspending over sulphuric acid, decomposed by means of sulphuretted hydrogen. The products consisted, however, chiefly of copper sulphide, with urea and ammonium sulphocyanide.

Further, an attempt was made to combine fulminic acid with the element silicon by passing a stream of dry silicon fluoride over argentic fulminate, kept moist by means of petroleum. Large quantities of argentic fluoride were at once formed, and the escaping gas, when collected and examined by introducing a light to the same, exploded with great violence.

Although the experiments when performed by the same method yield results which closely agree, it still remains an open question whether such a compound as silicon fulminate does in reality exist. Chlorine, iodine, and bromine were also employed, but chiefly gave rise to the substance known as chloropicrin and other bodies of an allied formula.

Experiments were also performed with a view of obtaining an ethyl compound, but these require further investigation before speaking definitely of them.

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A NEW METHOD FOR THE ESTIMATION OF CANE SUGAR IN SOAP.

By J. A. WILSON.

IN an examination of the best methods of determining soap adulterants, I have felt the want of a quick, rapid method, for the determination of sugar, which is frequently added to toilet soaps to the extent of 20—30 per cent.

The method of separation of the fatty acids by decom-

position with mineral acid, which converts the sucrose into invert sugar, with subsequent titration with Fehling's solution, gives fairly satisfactory results, but which are inclined to be too low owing to destruction of the invert sugar by the prolonged action of the mineral acid.

The best way of conducting the inversion process is to add to the weighed hot soap solution one or two c.c. of normal acid in excess, separate the fatty acids as quickly as possible, and carefully neutralise, then evaporate to 75 c.c. and invert the sugar by means of HCl in the usual manner; the estimation of the invert is then made gravimetrically.

In the new method we estimate the cane sugar as such by means of the polarimeter in the following manner :—
10 grms. of the soap are dissolved in a beaker in 150 c.c. of water at 80° C., and a saturated solution of magnesium sulphate added drop by drop from a pipette, stirring well till in slight excess. The whole is thrown on a capacious filter, and the magnesia soap washed three to four times with hot water containing a little $MgSO_4$. The filtrate and washings, which are slightly alkaline, are treated with very dilute HNO_3 till the alkalinity is very faint. Evaporate to 40 c.c., cool, add dilute HNO_3 till just acid, then a few drops of basic lead acetate and 2 c.c. of alumina cream ; dilute exactly to 50 c.c. and polarise the solution in a 200 m.m. tube. The number of angular degrees divided by 2·66 (if the rotation is for the D line) gives the grms. of cane sugar in the 10 grms. of soap taken. I have made the following experiments to prove the accuracy of the process :—

1. 10·165 grms. of a sample of transparent soap gave a solution, when diluted to 50 c.c., rotating 3·66 angular degrees for the D line, equal to 1·376 grms. sucrose, or 13·53 per cent.

2. The same soap on second test gave 13·48 per cent. The percentage as found by inversion by HCl and weighing as CuO was 13·33 per cent.

3. 10 grms. of a sample of soap containing no sugar, 2 grms. of absolute glycerol, and 1 grm. of pure cane sugar gave a solution rotating 2·55 angular degrees for the D line, which is equal to 0·96 grm., or 9·6 per cent instead of 10 per cent.

4. 10 grms. of soap (containing no sugar), 2 grms. of absolute glycerol, and 2 grms. of pure cane sugar, when treated by the above process, gave a solution, when diluted to 50 c.c., giving the rotation $(A)_D = +5·32$, the calculated activity being 5·33.

We consider these experiments quite satisfactory for all practical purposes. It will be noticed that the optical activity of cane sugar has been taken as working simply in a watery solution, whilst really we have a mixture of salts and glycerol, but the above experiments show that the rotation is not influenced to any appreciable extent by these foreign matters. The process is simple and can be worked in about two hours from the commencement.

Tottington Mills, July 7, 1891.

A NEW SOURCE FOR XYLOSE.*

By W. E. STONE and DUMONT LOTZ.

ONE of us, in applying the furfurol test to a variety of vegetable materials, in search of the pentose carbohydrates, or *pentans*, found that the "cobs" of Indian corn were especially rich in these bodies.†

In the preliminary test cited, by distilling the air-dried material with sulphuric acid of 1·254 specific gravity, and precipitating the furfurol thus obtained as furfuramide, the equivalent of 12 to 13 per cent of furfurol was obtained. This result, which quite equals that obtained under similar conditions from cherry gum and gum tragacanth, indicated that the corn "cobs" might compare favourably with the latter materials as a source of one or the other of the pentoses. Since the tests mentioned we have repeated the furfurol determinations, making use of a method proposed by Tollens and Chalmot, and privately communicated to one of us. By this method the material is distilled with hydrochloric acid of 1·06 specific gravity ; the furfurol thus obtained is precipitated from acetic acid solution with phenyl-hydrazine, dried in a current of dry air at 60°, and weighed as phenylfurfurazide. In this way somewhat higher results were obtained. One distillation of the air-dried material gave 21·89 per cent furfurol, and a second 22·36 per cent.

Our method of procedure was to extract the pentose carbohydrates from the material by means of strong alkalies, and then by hydrolysis convert them into the specific pentose.

Two and one-half kilos. of finely-ground air-dried "cobs" were digested, cold, with 12 litres of 1 per cent ammonia solution during about thirty hours, for the purpose of removing colouring matters. When drawn off the liquid was of a dark brown colour, but nothing was precipitated from it when several volumes of strong alcohol were added, showing that none of the gummy pentose carbohydrates had been extracted.

The residue, which was perceptibly lighter in colour than before this treatment, was next subjected to the action of a sodium hydroxide solution in order to effect solution of the gums. In his treatment of sugar-beet chips for the extraction of the so-called metapectic acid from which arabinose was first prepared, Scheibler used for this purpose quicklime.* Later, one of us by the same process obtained from the fermented residue of malt a gum which, upon hydrolysis, yielded both arabinose and xylose.†

Tollens and Allen have found, however, that caustic alkalies gave better results in the preparation of xylose from wheat-straw.‡

Accordingly, the residue left after extraction with ammonia received enough of a 2 per cent sodium hydroxide solution to cover it, and the whole was boiled during eight hours, the liquor becoming very dark coloured and mucilaginous. After standing eight hours longer the liquor was separated from the residue of fibre and insoluble matter by means of a press. Upon addition of two volumes of 95 per cent. alcohol to this liquor, a voluminous, dark brown, gummy precipitate was thrown down. This was several times washed with alcohol by decantation. Finally it was re-dissolved in a little water, to which some hydrochloric acid had been added, and then re-precipitated with alcohol. This treatment was repeated several times. The final result was an amorphous substance of light brown colour, which upon exposure to the air seemed slightly hygroscopic, and rapidly blackened. After drying over sulphuric acid this product weighed about 200 grms., or about 8 per cent of the material employed.

A small quantity of this gum was repeatedly dissolved in water and re-precipitated from an acid solution by means of alcohol, with the object of obtaining a pure ash-free product for further study. The last traces of ash were, however, very difficult to remove, and after some months the preparation still contained 0·76 per cent. Spectroscopic examination showed this ash to consist of sodium salts. Two portions of this gum yielded on distillation, respectively, 48 and 50 per cent. of furfurol. This partially purified material was noteworthy for its solubility in water and its rapid discolouration on exposure to the air. The greater portion of the 200 grms. of gum was heated in a flask with 2 litres of 2 per cent sulphuric acid for twelve hours, an inverted condenser being used to prevent concentration of the acid by evaporation.

* Contributions from the Chemical Laboratory of Purdue University.
† *Am. Chem. Jour.*, 13, 73.

* *Ber. d. Chem. Ges.*, 1, 58, 108.
+ *Ann. Chem.* (*Liebig*). 249, 243.
‡ *Ibid.*, 260, 289.

At the end of this time about 50 grms. of amorphous, insoluble matter remained in the flask. The acid liquor was filtered from this residue, neutralised with calcium carbonate, and evaporated to a thick syrup. Upon adding about three volumes of strong alcohol to this and boiling, a dark brown, tasteless gum was precipitated and removed, and the liquid after concentration yielded slowly a mass of dark coloured crystals.

After repeated washings and re-crystallisations, two successive portions of crystals were obtained, which were nearly white, sweet to the taste, and reduced Fehling's solution strongly. In all about 6 grms. of this product were obtained, or nearly 3 per cent of the 200 grms. of gum used. Probably an equal amount of sugar remained in the dark coloured and non-crystallisable mother liquors. The amount of this product obtained was disappointingly small in view of the promisingly preliminary indications. The syrups obtained after hydrolysis, however, contained much unchanged gummy matter, and crystallised only slowly and with great difficulty. It was also found subsequently that the extracted cobs still contained a very large amount of the furfurol-producing bodies. The caustic soda had evidently extracted only a very small amount of the *pentans*, or pentose gums, which accounts for the small yield of sugar. To characterise the product thus obtained, the specific rotation was determined, and its phenylhydrazine derivative prepared. Of the two portions of crystals, No. 1 showed the specific rotation $(a)_D = 19\cdot4°$; No. 2, $(a)_D = 19\cdot7°$. These numbers agree with sufficient accuracy with the specific rotation of xylose—$(a)_D = 18\cdot5°$ to $19°$—to identify both products as xylose, and show that this was the only pentose present. The phenylhydrazine compound was prepared in the usual way, had a normal appearance and behaviour, and showed the melting-point 159°—the approximate melting-point observed for phenylxylosazon (156°—160°). In distinction from the phenylarabinosazon, which has the same melting-point, this compound was distinctly lævo-rotatory, a property of the xylose derivative as shown by Fischer.[*]

These data add a new and, as we hope to show by a repetition of the above work, a fruitful source of xylose to those already known, and emphasize once more the reliability of the furfurol test for the recognition of such materials.—*American Chem. Journal*, Vol. xiii., No. 5.

ON TERMINAL SPECTRA OBSERVED
IN VACUO.

By E. E. BROOKS.

In the CHEMICAL NEWS, vol. lxii., p. 230, November 14th, 1890, I gave a brief preliminary notice of these spectra in a paper on the " Phosphorescence of Lithium Compounds," and as I believe they have never previously been mentioned I now propose to describe them more fully.

Terminal spectra are of the same order as spark spectra obtained in air, their interest mainly lying in the method by which they are obtained, which is usually as follows :—

A number of small vacuum tubes are prepared, 2 or 3 inches long and half an inch diameter, one terminal being a very small plate of aluminium, not more than $\frac{1}{4}$ in. square, and usually covered on one side by a mica screen, the other terminal being either the same or a small spiral of fine wire. Some metallic salt or compound is introduced, and the tube exhausted to the required degree, and then sealed up. To use it, a little of the contents is made to rest on one of the terminals by shaking or jerking the tube, and the terminal (made negative) is examined with the spectroscope while coil discharge is passing, lines due to the metal being then seen superposed upon the spectrum due to the gas.

I at first hoped that the method would enable me to prepare standard tubes containing salts of various metals, which would give metallic spectra as readily and permanently as vacuum tubes containing gases, and with a few metals this is possible, but with the majority the method is inferior to the ordinary spark process in air.

The metallic lines are easily distinguished from the gaseous lines seen at the same time. The latter are steady, extend the whole width of the spectrum, and are of equal brilliancy throughout; while the former flicker more or less, and often appear in flashes, and usually only extend partly across the spectrum. The C and F lines of hydrogen are almost always very strong.

It will be seen that these spectra are quite distinct from the phosphorescent spectra first studied by Mr. Crookes, which are of a totally different character, and are only visible at a degree of exhaustion much beyond the limit at which these spectra disappear.

Some fifty vacuum tubes of various designs were made and used, experiments being made with carbon terminal soaked in solutions of salts, with movable terminals with fused coatings, and with terminals of different metals. The following results were obtained, using a coil giving about 1 inch spark, which was hardly powerful enough for the work.

Lithium.—These spectra were first noticed while examining a specimen of $LiNO_3$ *in vacuo*. The salt was heated with a lamp until partly volatilised, a portion condensing again on the aluminium terminals of the tube. On passing the discharge, the negative terminal shone with a deep red light, which was found to give the red and orange lines very strongly. All the salts of this metal give very good results.

Sodium.—The D lines are as common an impurity in these spectra as they are in spark and flame spectra, and the reaction seems almost as delicate. Using any sodium salt, the terminal is covered by an intense yellow glow, and the D lines are always strong. A slight increase of strength in the discharge brings out the double green line, and the double red line can be seen occasionally. NaCl has a bright greenish phosphorescence in a high vacuum.

Cæsium.—The two blue lines (a and β) are seen occasionally when the chloride is used, but not very readily.

Barium.—$BaCl_2$ gave readily a good and distinct spectrum, which remained visible in higher vacua than usual. The following lines were identified :—

6496, 6141, 5853, 5534, 4933, 4553, and (probably) 4165. $BaCl_2$ phosphoresces bright greenish-blue in a high vacuum.

Calcium.—$Ca(NO_3)_2$ was used. The terminal shone with a strong red glow, and brilliantly white incandescent points broke out here and there. The orange and green bands came out very distinctly, and the bluish violet line 4226 was well seen in the flashes.

Strontium.—The chloride and nitrate were used, but with rather poor results. The red lines were almost invisible, green and blue lines were glimpsed in flashes, but the only one I could identify with certainty was the blue line 4607, which was easily seen.

Magnesium.—Using the sulphate or nitrate, the triple green lines came out strongly at times, but the effect was rather uncertain. Very intense green points occasionally seen on the positive terminal.

Zinc.—The oxide and sulphate were used. The red line 6360 was very strong, and three green lines, 4810, 4721, 4679, were also seen. ZnO phosphoresces in a high vacuum with a peculiar greenish yellow glow, and $ZnSO_4$ gives a bright bluish phosphorescence.

[*] *Ber. d. Chem. Ges.*, 23, 355.

Cadmium.—With the iodide two lines came out very distinctly at 5085 and 4799. In a high vacuum the salt gave a bright light yellow phosphorescence, with traces of brown and red. Heating the salt with a spirit lamp caused a whitish coating to condense on the sides of the tube, and when the discharge was again passed, this coating shone with a very bright greenish yellow light, similar to the phosphorescence of German glass, but evidently not due to the glass of the tube, as the latter was made of lead glass.

Lead.—$PbCl_2$ was used. A good spectrum easily obtained, and for the first time metallic lines were noticed on the positive terminal. A jet of light shot out from one side of the negative spiral wire, and the glass on which it impinged became quickly covered with a thick dark coating. All the following lines were visible at the positive terminal:—

5607, 5546, 5372, 5043, 4386, 4245, 4020.

Silver.—With either $AgNO_3$ or $AgCl$ two strong green lines were seen at 5464 and 5208, but the nitrate is rather inconvenient to use on account of its ready fusibility. The chloride gave a curious effect in a high vacuum. When the discharge was first passed, the white chloride shone with a bright light green phosphorescence; but under the influence of the discharge it immediately darkened, and as it darkened the phosphorescence faded rapidly away. By shaking the tube a fresh surface of white salt was exposed, thus renewing the phosphorescence, which again quickly faded, and in this way the effect could be repeated a number of times.

Mercury.—Using Hg_2Cl_2, the negative terminal and the space around it shone with a strong green light, almost like a flame; but the salt volatised very rapidly, and the condensation on the sides of the tube soon prevented observation.

A sub-nitrate was more convenient in use, and gave a similar result. On the negative plate were seen green flashes of light, and when the spiral wire was made negative the green glow was very intense. There was a good deal of continuous spectrum, and the green line 5460 was very strong. Two other lines were well seen—one 5790, the other probably 4358.

Thallium.—The sulphate was used and always gave very good results. The terminal was surrounded by green flashes of light, and the line 5349 was very sharp and distinct.

I failed completely with rubidium and potassium, although several attempts were made with various of their salts.

With aluminium oxide, Al_2O_3, I could see in short flashes a sharp line spectrum, but could not keep it visible long enough to fix the position of the lines.

Phosphoric anhydride gave a similar result. A good spectrum could be seen, but only in short quick flashes.

Boric anhydride gave feeble results. I could just distinguish the green bands of the oxide, which were very faintly visible.

A number of compounds of other metals were tried without much success, although in several instances there were indications that a slightly more powerful discharge would have been more effectual.

The general conclusions arrived at are as follows:—

The metallic lines have their origin in very small flickering luminous points, which appear on the surface of the terminal, and are not seen in the negative glow surrounding the terminal, except in the case of very volatile metals. These luminous points seem to be minute portions of the material momentarily raised to a very high temperature.

The best results are obtained with the more volatile metals.

The nature of the acid or state of combination does not seem to be of primary importance. All the compounds of Li or Na, for instance, seem to answer equally well.

Increasing strength of discharge increases effect, and as a rough general rule, the point of maximum brilliancy appears to be near the pressure of least resistance, and this indicates that density of current has an important influence.

No special advantage was obtained by introducing condensers into the secondary circuit.

These spectra can only be obtained at the negative terminal.

It is true that in one or two instances metallic lines were observed at the positive terminals, but I am inclined to think, from the general results, that this was due to a reverse current, as my coil at certain pressures and with terminals of equal size will show two negative poles in the same tube, the discharge being evidently alternating.

When a tube is first made it is sometimes rather difficult to lodge a little of the salt on the terminal; but immediately the discharge passes the coating becomes strongly adherent, and continually increasing with use, and in several cases the tube became non-conducting, apparently because the coating of salt was too thick to permit discharge to pass.

The spectrum effect frequently faded while the terminal was under observation, although it was still thickly coated with salt.

Jerking the tube so as to cause a fresh layer of material to reach it usually restored the effect, and was often accompanied by an instantaneous increase of brilliancy in the gaseous glow in the body of the tube.

The phenomena of electrical evaporation, as recently described by Mr. Crookes in the case of metals, was very marked in some of the experiments with compounds. Bodies like As_2O_3, P_2O_5, and Hg_2Cl_2 immediately volatilised when the discharge was passed, and condensed again in thick coatings on the sides of the tube.

The main object of my work was an endeavour to obtain information as to the nature of the actions which occur at the negative terminal during discharge, of which at present very little is definitely known. I am inclined to think that the spectral lines are only obtained when the discharge actually travels through a portion of salt in its passage from terminal to gas; and as the discharge through the salt must be of a disruptive character, the action is analogous to that which occurs in ordinary spark spectra in air. The effect of the spark in air is to volatilise and destroy the portions of salt in its path, and it therefore becomes interesting to inquire whether the vacuo discharge produces similar decomposition effects. It is evidently not sufficient that particles of salt should be raised to incandescence by the heat of the discharge; the metal must be actually in a state of vapour before sharp, bright lines can be obtained.

I have at present scarcely touched this part of the work, but the coatings on the terminals often became blackened and discoloured, and dark coatings on the glass were frequently met with. In the case of fairly stable salts I have been unable to detect the slightest trace of a rise of pressure in the tube, such as might be attributed to decomposition. The following experiment, however, seems to indicate that such an effect may occur to a slight extent:—A tube containing thallium sulphate, which had been in use during six months, was opened. The negative terminal was partly covered with a deep black powdery substance, the other terminal being nearly quite clean. The terminal was well washed, and then placed in water, which was slightly acidulated by means of a glass rod dipped in H_2SO_4. The black coating immediately began to dissolve, accompanied by evolution of gas. When it had all disappeared the gas bubbles ceased also, and the solution gave the reactions of thallium; but the amount of black powder obtained was very small, especially in relation to the number of times tube had been used. I hope to experiment further in this direction.

Countess Street, Leicester.

CONTRIBUTIONS TO MICRO-CHEMICAL ANALYSIS.*

By H. BEHRENS.

(Continued from p. 5).

IF a loss of precipitate is not an object we may have recourse to the method of filtration recommended by Streng by means of narrow slips of paper. The port object with the drop which is to be filtered is laid upon a small board having a slope of about 1 : 20 ; a second is pushed up to the margin of the board so that the vertical distance of the two from each other is about 5 m.m. They are then connected by means of a slip of filter-paper of the shape of a Y, the arms of which are moistened so as to adhere to the upper glass, and the liquid to be filtered is brought into contact with the paper. The dimensions proposed by Streng, 2 m.m. in breadth, and 25 m.m. in length, may be reduced to 1·5 m.m. and 10 m.m. The quantity of liquid which is retained in and below the slip of paper amounts then to 5 m.grms. The precipitate does not fare so well, as much of it—if washing is necessary the greater part—soaks into the paper. This loss is diminished if an approximate separation can be effected by means of a wire as described above.

There remains, undeniably, room for improvements which will be very welcome if we do not lose what is good in our quest for something better. I have kept in view the small bulk of the apparatus, and the consequent possibility of working with it in all places, and at the same time the economy of time by avoiding unnecessary preparations. It must not be thought that especial genius is needed in order to work expeditiously and well with the simple means above described. Correct observation and independent thought are certainly needed and the operator must learn to work with little apparatus. All this applies, however, just as well to blowpipe analysis. If a fair attempt is made I am convinced that an experienced analyst who has made occasional use of the microscope will encounter no more serious difficulty with micro-chemical analysis than he once did with the blowpipe.

Reactions.

I.—*Potassium.*

1. With platinum chloride. Lemon-yellow sharply developed octahedra of K_2PtCl_6, refracting light strongly, sometimes assuming a hexagonal structure by flattening and combination with ∞ O ∞. Size 10 to 50 micro. If rapidly deposited sometimes combined in threes and fours in the shape of a clover leaf or of a cross. Solubility 1 : 100. Limit of the reaction 0·0005 m.grm. K.

Use a strong solution of platinum chloride, which when drying up must not deposit octahedral crystals. A drop of this liquid of about 0·2 m.grm. is placed on the specimen drop, which should be neutral or faintly acid. In dilute solutions the yellow octahedra only form after a few minutes along the margin. An excellent reaction, if the presence of cæsium, rubidium, and ammonium is excluded. An excess of strong acids, especially of sulphuric acid, reduces the sensitiveness of the reaction, but may be counteracted by an addition of sodium or magnesium acetate.

2. With phosphomolybdic acid. Minute crystals very similar to those described under 1 ; combinations of O with ∞O mostly globular, refracting light strongly, principally accumulated at the margin of the drop. Limit of the reaction about 0·0003 m.grm. K.

In using phosphomolybdic acid it must be noted that its solution on evaporation yields fine yellow octahedra, even if no alkali is present. The octahedra of the pure acid are sharply developed with straight edges, measuring 30—60 micro., whilst those of the potassium compound are rounded and about three times smaller. The reagent must be added freely ; the sample drop is acidified

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* *Zeit. Anal. Chemie.*

with hydrochloric or nitric acid, and a large drop of the reagent is added. It is useful for strongly acid solutions, but it must be used with caution, as besides potassium it precipitates cæsium, rubidium, ammonium, and lithium.

3. With bismuth sulphate. Colourless hexagonal discs which are slowly developed to stellar, rhombohedric structures (R·—R·OR of 30—60 micro.), limit of the reaction 0·0002 m.grm. K.

Basic bismuth nitrate may be used, dissolved in nitric acid with the addition of a little sulphuric acid. The solution to be tested must first be concentrated. Nitric acid delays the reaction, but does not prevent it except in very large excess. Ammonium behaves like potassium with bismuth sulphate. Sodium is also precipitated, but in a quite different form.

4. With silicofluoric acid. Very small cubes with faint outline 10—20 micro.

This reaction proposed by Boricky is not recommended on account of the smallness and paleness of the crystals, but it sometimes makes its appearance unintentionally during micro-chemical work.

II.—*Sodium.*

1. With uranylacetate (Streng). Pale yellow sharply developed tetrachloride of about 50 micro. Limit of the reaction 0·0008 m.grm. Na.

As a reagent we use a solution of uranylacetate in acetic acid. The sample liquid is to be strongly concentrated as the reaction is very faint at a dilution of 50. Strong acids should be expelled by evaporation, ammonium acetate being used only in cases of necessity, as an excess of ammonium salts interferes with the reaction. Streng adds that platinum chloride also interferes, which must be remembered with reference to potassium.

2. With uranylacetate and magnesium acetate (Streng). Rhombohedric crystals almost colourless ; chiefly

$$OR·R·—2R· \frac{8}{3} P_2,$$
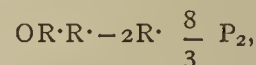
according to the position and the predominance of tetrahedral, dodekahedral, rhombic, or hexagonal structure. Size up to 120 micro. Limit of the reaction 0·0004 m.grm. Na.

This reaction is produced under the same conditions as 1, if along with sodium metals of the magnesium group are present in excess.

3. With silicofluoric acid (Boricky). Hexagonal discs and short columns of the combination ∞P·P, measuring as much as 70 micro. From less dilute solutions there are thrown down elegant, six-leaved rosettes, of 80—120 micro. in size. Solubility 1 : 150. Limit at 0·00016 m.grm. Na.

Instead of silicofluoric acid may be used ammonium-fluosilicate if a granule is placed in the moderately acid sample. More massive crystals of sodium fluosilicate have a faint rose colour. Platinum chloride does not interfere. In highly diluted solutions the reaction appears only as evaporation proceeds.

4. Bismuth sulphate. Colourless hexagonal rods 20—80 micro. Limit of the reaction 0·00004 m.grm. Na.

Compare potassium No. 4. The reaction is serviceable for the simultaneous detection of potassium and sodium. To this end a solution of bismuth sulphate in dilute nitric acid is spread out in a layer of 0·3 m.m. in depth, and the sample in question is placed in the middle of the extended drop either as a solid or as a thick paste (sulphate). A short heating to 50—60° accelerates the precipitation of the sodium double salt which collects round the specimen. The discs of the potassium double salt appear later and diffuse themselves over the whole preparation.

Haushofer's test, potassium pyroantimoniate, did not give good results. The reaction was tedious and the crystals not well defined.

(To be continued).

THE SEVENTH INTERNATIONAL CONGRESS OF HYGIENE AND DEMOGRAPHY.

NEXT month will witness a gathering which promises to be the leading scientific event of the season, and which will, we hope, leave its mark behind in the shape of permanent results. Looking at the papers already announced, we may venture to doubt whether they can receive due discussion in the time allotted. We must hope, to this end, that the readers of papers and other speakers will not indulge in self-advertisement, such as is often introduced on such occasions; and that they will, above all things, eschew the introduction of political considerations, for which two, at least, of the sections might supply temptation.

Our attention is naturally drawn chiefly to Section V., "Chemistry and Physics in Relation to Public Health." This section will hear and consider the following papers :— On Tuesday, August 11, a memoir on "Smoke and its Effects," by Dr. W. J. Russell, followed by a paper on "The Air of Large Towns, and Methods for its Analysis," by the Manchester Field Naturalists' Society, and a paper on the "Means at our Disposal for Preventing the Emission of Smoke from Factories and Dwelling-Houses," by Mr. A. E. Fletcher, H.M. Chief Inspector of Alkali Works, &c. Dr. C. Merdon Williams will take part in the discussion with regard to "fog from a hygienic point of view."

On Wednesday, August 12, there will be read papers on that much-disputed subject the "Treatment of London Sewage," by Dr. Dupré, F.R.S.; "Outline of the Various Chemical Processes for Purifying Sewage," by Dr. J. C. Thresh; "The Duties of a Locality to Secure the Nitrogen of its Sewage for the Benefit of the Nation," by Dr. A. Carpenter. It need scarcely be said that if the utilisation of such nitrogen is proved to be a duty, all those processes which aim at carrying sewage or sewage precipitates into the sea, and no less all those processes in which its constituents are converted into cements or otherwise destroyed as such, are at once condemned. Dr. A. Carpenter further contributes a paper on the power of soil and vegetation combined to destroy disease germs, and to prevent the possibility of a spread of enteric disease in consequence of sewage farms.

Herr Margraf, of Berlin, promises a paper, though he may possibly be unable to be present and take part in the discussion.

On Thursday, August 13, Prof. Dr. Lehmann, of Wurzburg, will bring forward a paper on "The Hygienic Importance of Copper," a subject as yet far from having been fully elucidated. There follow two other papers on subjects of great importance bearing upon public water-supply: "The Importance to be Attached to Magnesia in Drinking-Waters," by Prof. P. F. Frankland, F.R.S., and "The Action of Water on Lead," by Dr. J. H. Garrell.

Next follows a paper on "The Antiseptic Treatment of Food," by Mr. O. Hehner, and one on "The Effects of the Respiration of Carbonic Acid on Man," by Dr. W. Marcet, F.R.S.

On Friday, August 14, will be read an "Introduction to Meteorological Subjects," by Lieut. Strachey, F.R.S., followed by papers on the "Influenza . . . (?) of London," by Sir A. Mitchell and Dr. Buchan, and "Hygienic Improvements in the Manufacture of Bread," by Mr. J. Goodfellow.

It is further expected that papers for this section will also be contributed by Prof. Liebreich, of Berlin, and Prof. Lunge, of Zürich.

We see with regret that much of the matter to be taken into consideration in Section VII.—Engineering in Relation to Hygiene—is in its character distinctly chemical and physical, such as the chemical and electrical treatment of sewage, the quality of potable water, its purification and the pollution Lof rivers—subjects which can only be discussed by chemists, and on which chemists alone are qualified to adjudicate.

THE PROGRESS OF CHEMICAL THEORY: ITS HELPS AND HINDRANCES.*

By Dr. PERSIFOR FRAZER, Prof. of Chemistry.

THE long chemical war against phlogiston had been fought and won, and the thought of experimenters was turning in a new direction which was to institute a new war lasting only a little less long than the last, but the difference between the two cases was that whereas the phlogistic theory hung like a pall over the whole science, obscuring during its continuance the entire field; in this case the question in dispute was as to the ultimate constituents of matter, and none of the many views entertained on these questions interfered with the classification and assimilation of the myriads of facts which experiment and research were eliciting. This war, therefore, while it will serve to illustrate that the most eminent chemists share with the rest of the world the weaknesses of our common humanity, did not materially retard the progress of the theory of chemistry.

Proust (1755—1826) announced the unchangeable proportions by weight in which substances combine together; and that if they combine in more than one proportion it is by leaps and not gradually, as the water of the ocean becomes little by little more charged with salts brought down to it by the rivers. This was a great and pregnant discovery which at once led the way to the new field of battle, but the strangest thing about this announcement is that it was vehemently attacked by Berthollet (like Proust, a native of France), in a proposition which a little later seemed nothing but a stupid blunder or obstinate opposition, and yet in Berthollet's contention lay a precious truth only recently recognised and placed in its proper place.

Briefly, the skirmish between these two men was this. Proust discovered that the relative proportion to each other by weight of carbonic acid and copper in carbonate of copper was constant; no matter in how great excess one or the other of these bodies was present, the weight of the carbonate of copper was the same, and the weight of each constituent in it was invariable. For instance, substituting the accurate weights which better methods and apparatus have enabled chemists to obtain for the inaccurate approximations then made, in 123·4 grms. of carbonate of copper (there were always 63·4 grms. of copper, and 60 grms. of carbonic acid). It made no difference whether these weights of the two elements respectively, or whether two or three times as much of one with the above weight of the other were made to combine; the result was always that 123·4 grms. of the compound were found, and the excess of either element remained uncombined.

With tin and iron there were two proportions by weight in which each of these elements combined with oxygen, but there were no insensible passages from one to the other. Thus there was a compound of oxygen and tin in which 119 weight-units of the latter combined with 16 of the former; and there was another in which 119 tin combined with 32 of oxygen, but there was none in which the 119 weight-units of tin combined with any number of weight-units of oxygen between sixteen and thirty-one.

Berthollet (1748—1822) maintained, on the contrary, that if different masses of two elements are brought together, there will be found in the compound more of that constituent which was in greater quantity before the union. On account of the high position which Berthollet held in the chemical world this view received respectful, though silent attention, for few of the masters of the science were won over by it; because Richter, Klaproth, Vauquelin, and Wenzel had placed the constancy of acid and base in a compound of the two beyond all question.

Proust, however, took up the gauntlet and followed each separate publication of Berthollet by a refutation based upon careful experiment. This lasted for eight years, or from 1799 to 1807, and was settled apparently for ever when Proust, by repeating some of Berthollet's own experiments on the successive stages of oxidation showed that his opponent had mistaken a percentage of water for a percentage of oxygen.

But Berthollet's main idea that the mass and the affinity were inseparable factors in the formation of a compound, after having been crushed to earth, was to rise again in more recent times by the labours of his countrymen of almost similar name, Berthelot and St. Gilles, and by Guldberg and Waage; but they showed, not that the proportion by weight of the compound, but that the rapidity of the reaction was affected by the masses of the constituents.

This dispute and the rise and fall of a theory was only a slight skirmish, which was preliminary to the general engagement. It had an admirable effect on the science, widened men's views, proved that the weapon of the future was to be a carefully conducted experiment; and without doubt ripened the next great discovery which was then about to be announced.

John Dalton (1766—1844) was led to the happy thought of taking the data of the weights which Proust had announced as those in which tin, iron, oxygen, &c., combined, and reducing them to their simplest proportions. Proust had found that some arbitrary number of grms. of tin (say, for example, 119), combined either with 16 or with 32 grms. of oxygen, and with no other weights. Dalton showed that the weights of oxygen in these two compounds were to each other as 1 to 2.

In the same way the different weights of sulphur which entered into combination with a given weight of iron were to each other as 1 to 2. And he found that this held for all cases where two constituents combined with each other in more than one proportion.

Thus, if the amount of hydrogen in olefiant gas or ethylene and marsh gas or methane are compared, they are to each other as 1 to 2. By numerous examinations of this kind, in all of which he found this simple relation, he was led to formulate his atomic theory, some of the more important propositions of which may be thus condensed. (1) Every element consists of similar atoms of fixed weight; (2) Chemical combinations are made by the union of the atoms in the simplest proportions. The atomic weight of a compound is equal to the sum of the atomic weights of its constituents. He supposed all the atoms to be spherical and to be surrounded by heat spheres (!)

It should be mentioned in passing that Higgins had said in 1789 that chemical smallest particles were united to form compounds in simplest proportions, but as he never adduced any proof of this, the merit of the discovery belongs to Dalton by the law of possession already alluded to before, viz., that in natural science not only must a truth be announced, but some reason for it must be given.

The immediate result of his postulates was that Dalton set out to establish a scale of atomic weights for the elements. Among minor postulates of his which have not lived till our day, but which were natural enough at a time when there were no means of obtaining certainty as to the questions of the number of atoms entering into combination, &c., was this, that if only one proportion by weight of a combination between two elements were known, it must be supposed that the number of atoms entering into this combination was one from each element. If two were known, then that in which the least weight of one combined with the least weight of the other must be considered 1 to 1; when with double this weight of the other the proportion must be 1 to 2, &c. In Dalton's time only one combination between oxygen and hydrogen was known, viz., water, and he assumed this to be composed of one atom of H to one atom of O. As H was

and is yet the lightest element known, he assumed its weight as one. By the imperfect methods then available, he determined the weight of O which combined with it to form water as 6·5 (in reality it is 7·98 if H = 1).

Ammonia, which was the only compound of H and N known to him, and in which he also assumed one atom of each element, gave him the number 5 for the atomic weight of N. By accurate methods it should be 4·66. In the lowest compound of carbon and oxygen known, carbonous oxide, he found the atomic weight of carbon 5·4 calling oxygen 6·5 (the right figure is 6).

All his figures were wrong as we now believe because of his false assumption of the constitution of water (not to speak of his imperfect methods of analysis), yet the accuracy which he attained was surprising for his epoch and the invigorating effect on the science was as great as if all his numbers had been absolutely correct.

Humphry Davy (1778—1829), the great discoverer of the alkaline metals and earths, who first announced the elemental character of chlorine, and by his discovery of the halogen acids seemed to have overthrown Lavoisier's dictum regarding the invariable presence of O in all acids —Davy, the discoverer of the safety-lamp for miners, first announced his belief that chemical affinity and electricity were the same force. This idea was erected by Berzelius later into the splendid structure which he called the electro-chemical theory. Neither Davy nor Wollaston believed that Dalton's experiments had succeeded in establishing the nature and characters of atoms, but contented themselves with Wollaston's theory of "equivalents," without seeking to define how much matter entered into combination.

Their theory was that the atomic weights of Dalton were merely a series of arbitrary numbers, showing the respective quantities of different elements which were equivalent to each other in combining each with a third.

Wollaston's name of "equivalents" took root later after the apparent failure of Berzelius's theory to account for all the facts, and was the shibboleth of a long period of timidity and vacillation in chemical theory, which marked the reaction of thought when it was feared that the allurements of a beautiful system and the powerful influence of a great authority had drawn the representatives of the science away from sure ground. This period of intellectual cowardice was very tantalising and very confusing to those who pursued their studies during this period, but in the end it was an advantage to the science by letting the field lie fallow for a time, and making it thus the fitter to receive and develop the seed which finally was sown upon it.

In all cases where the development of a science has been rapid, it is found that the great minds are clustered together, and that the great discoveries occur in succession to supplement each other. It was stated that the discovery by Black originated pneumatic chemistry or the chemistry of the gases. In this field the discoveries of Cavendish, Priestley, and Scheele were made, but with the wider view given by Lavoisier to the science, the study of the gases was abandoned for the study of other solid and liquid compounds. But Gay-Lussac (1778—1850) devoted himself to pneumatic chemistry and accomplished in it what supplemented the work of Dalton, and prepared the way and assisted the researches of Berzelius.

In 1805, in conjunction with Alex. von Humboldt, Gay-Lussac established the fact that exactly two volumes of H combine with one volume of O to form water.

He showed the simple relations of the volumes of combining gases to each other and to their compound; he showed the effects of temperature on gases, and how it must be considered in connection with the Boyle-Mariotte law of pressure. His conclusion was that "The specific gravities of gases are proportional to their atomic weights, or are simple multiples of them."

Avogadro, an Italian chemist and physicist, attracted by the discoveries of Gay-Lussac, had, in 1811, deduced from the Boyle-Mariotte law that in equal volumes of two gases at the same pressure and temperature must be contained an equal number of physical particles. It was such a small step from these two beautiful generalisations to the conclusion that the smallest physical parts of elementary gases not being indissoluble must contain more than one atom, and that, therefore, here was proven the physical smallest parts, and the still smaller chemical smallest parts which are capable of entering into combination. But though Avogadro announced this conclusion in 1811, it was long years before it was taken up and embodied in the theory of the science. Gay-Lussac furthermore, by his work on iodine and cyanogen, laid the foundation of the "radicle," as his experiments on the action of chlorine on oils did the same for the "substitution theory." He is also the inventor of the method of volume analysis or titrimetry.

J. J. Berzelius (1779—1848) offers a life history such as few have been seen since the beginning of the world. It seemed as if the tangled skeins of nature's most intricate clues were straightened and cleared in his hand as if by magic; and the marvel of the magnificent work which he left as a monument to himself, his country, and the science to whose cause he was devoted, is that hardly a line of it needs to be erased, and the corrections of his constants are decimals representing the greater accuracy of apparatus at the present day.

In 1812 he created a new mineral system, in which the combination of the elements in multiple proportion was clearly indicated. His improved methods of analysis served to enable him in 1814 to show that also in organic chemistry this law prevailed. The atomic theory was made by him the guiding principle for the science. He explained the union of elements by the polarities peculiar to their atoms, and his electro-chemical theory founded upon this hypothesis brought him to the dualistic view of the combination of matter.

The reason why so little of his work needs to be changed is that he based everything upon investigation and experiment. The results which he achieved here will remain, no matter what theory may be the final outcome of further advance. He saw at once that Dalton's rule for determining the relative number of atoms in a compound was arbitrary and he pronounced it so. With the help of Gay-Lussac's discoveries of the gas volume relations and his own discovery of the oxygen law of relation between the acid and the base, he was enabled to draw correct conclusions as to at least 2000 bodies which he had personally analysed. He considered the unit volume represented by the atom, and he deduced the constitution of bodies by weight and by volume (as, for instance, water) as we understand them to-day. It is only fair to observe that Berzelius himself, in spite of his strong belief in the power of the volume theory to assist the investigator to a knowledge of the true atomic relations of a chemical element, recognised its limitations and rejected altogether the efforts to apply it to bodies which could not be studied in the gaseous state.

This is only just to bear in mind, because an onslaught against the splendid structure which his skilful hands had erected was caused by a mistaken notion as to Berzelius's real views of the atom volumes. This onslaught caused the paralysis of the faculty of speculation for many years among chemists, converting one of the most enchanting and exciting fields of discovery into the mechanical record of dry facts, which it was contrary to the fashion of the day to seek to unite under any common cause. Had Berzelius's teachings been properly understood and heeded there had been no occasion for this panic, and the last days of the grand old Pioneer would not have been embittered by the thought that the labour of his life, which was good work, was doomed to destruction.

The atom values which he had obtained in 1818 are given herewith.

				Berzelius.	Correct.
C	..	..	..	12·12	12·0
O	..	..	..	16·0	16
S	..	..	..	32·3	32·06
Pb	..	..		416·0	206·95
Hg	..	..		406·0	200·00
Cu	..	..		129·0	63·4
Fe	..	..		109·1	56·0
Na	..	..		93·5	23·05
Ka	..	..		157·6	39·11
Ag	..	..		433·7	107·92

The reason that the values he obtained for the metals were so much higher than ours now, was that he then doubted the occurrence of other oxides than MO, MO_2, MO_3, &c., M standing for the metal. Instead of FeO, Fe_2O_3, he wrote these compounds FeO_2, FeO_3, and consequently his percentage of iron was doubled. For similar reasons the metals K and Na received four times their normal weight, since he regarded the compound, which we know now as K_2O_4, as KO_3. Some years later he modified this position, admitting the existence of M_2O_3, and his table then conforms nearly to the present. In his further classic work of determining the atom weights, he was assisted by the beautiful discovery of Dulong and Petit in 1819, that the atoms of all elements have the same capacity for heat, or that the product of the specific heat into the atomic weight gives a constant quantity.

Mitscherlich, a student of Berzelius, discovered that compounds of different elements which were similar in the number of atoms, the equivalent of water, &c., were isomorphic in crystallisation.

For example, in the phosphorus and arsenic salts only those which had like composition and like number of equivalents of water were isomorphic. Berzelius used both of these as guides, but showed a preference for the dictum of his former scholar. In his latter table of atomic weights of 1826, Berzelius corrected all but the alkali metals, which he still considered united to oxygen in the proportion of 1 to 1.
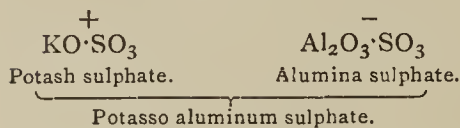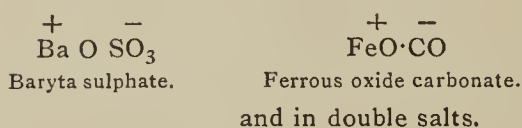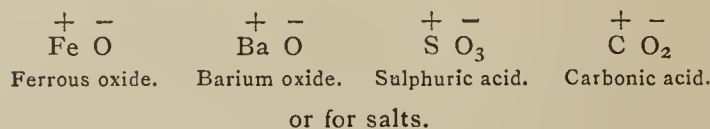
It will be recalled that Sir Humphry Davy and his school had pronounced chemical inseparable from electrical activity. He had shown that when a compound was decomposed by the electric current, and the separate constituents collected at the opposite poles (as, for example, sulphur and copper), these substances when rubbed or electrically excited showed opposite kinds of electricity: the substance at the negative pole showing positive, and that at the positive pole negative electricity. If the separate constituents (such, again, as sulphur and copper) were heated, the heat increased their electrical tension up to the point where they combined, and then all electrical activity ceased, the opposite kinds neutralising each other.

In conducting the current into the compound, its constituents received again electric polarity, and separated to the respective poles which attracted them.

Berzelius first stated his electro-chemical theory in 1812. His fundamental conception was that the atoms of bodies are electric, and therefore have at least two poles which generally are different in strength, and following this difference the elements which these atoms compose are electro-positive or electro-negative. This predominance of one kind of electricity extended to compounds, although necessarily more feeble in these. Compounds, according to this view, are the results of the attraction of the unlike poles of the atoms; and if in the compound there is a preponderance of one kind of electricity, this is because the atoms having this kind were more strongly polar than those having the other. Oxygen, as the most electro-negative of all bodies, was his criterion of the characters of the elements with which it combined. If the compound containing the least oxygen was basic, then the body combining with oxygen was electro-positive. If the oxide were an acid, then the element was electro-negative.

On this plan he arranged a table of elements in the order of their polarity. Of course it followed that any body in this table was electro-positive to all the elements on one side of it, and electro-negative to all those on the other.

His dualistic scheme followed as a matter of necessity, the two parts (whether two elements or acid and base) having opposite polarities. Thus :—

$$\overset{+}{Fe}\ \overset{-}{O} \qquad \overset{+}{Ba}\ \overset{-}{O} \qquad \overset{+}{S}\ \overset{-}{O_3} \qquad \overset{+}{C}\ \overset{-}{O_2}$$

Ferrous oxide.   Barium oxide.   Sulphuric acid.   Carbonic acid.

or for salts.

$$\overset{+}{Ba}\ \overset{-}{O}\ SO_3 \qquad \qquad \overset{+}{Fe}O\cdot\overset{-}{CO}$$

Baryta sulphate.   Ferrous oxide carbonate.

and in double salts.

$$\overset{+}{KO\cdot SO_3} \qquad \qquad \overset{-}{Al_2O_3\cdot SO_3}$$

Potash sulphate.   Alumina sulphate.

Potasso aluminum sulphate.

Berzelius carried his dualism and his electro-chemical theory into organic chemistry. In 1813 he had discovered a simple relation between the elements composing the organic acid and the oxygen of the base, and had proved the combination in multiple proportions in organic chemistry, and it was he who recommended the study of organic bodies in their combinations with inorganic.

He supposed organic, like inorganic, bodies to be binary in constitution, but with compound radicles instead of simple elements. This was Lavoisier's idea. Gay-Lussac had characterised alcohol as consisting of ethylene and water ; sugar as carbon and water. Döbereiner called oxalic acid a compound of carbonic acid and carbonic oxide. Berzelius opposed this conception as inconsistent with his electro-chemical theory. He could not acknowledge the existence of oxygen radicles. Yet the probability of such radicles was rendered strong by the discovery of organic bodies containing the same numbers of the same elements, yet exhibiting very different properties. This could only be explained by supposing that the proximate constituents were different.

Wöhler, Liebig, and Berzelius, after much hesitation, accepted the fact above referred to, and the latter designated the phenomenon as one of isomerism. Liebig and Wöhler had shown that a constituent of the oil of bitter almonds remained unchanged throughout a number of reactions, and this compound, of which the composition was $C_{14}H_{10}O_2$, they called benzoyl. (It is now called dibenzoyl or benzil).

At first Berzelius was disposed to accept this as an organic compound radicle, but reflecting that it must play the electro-positive *rôle*, although containing oxygen, he finally rejected this hypothesis, which he deemed inconsistent with his electro-chemical and dualistic theory ; and he was led to the assumption of arbitrary radicles containing no oxygen, of which the formulæ, when written together, completely obscured the intimate relationships which existed between classes of salts. This was Berzelius's first fault, not so much due to his vanity as to the feeling which was well founded that the scheme he had with such infinite pains established was right ; that it was being destroyed on theoretical grounds which, although he could not then satisfactorily answer them, with the instinct of a great genius he felt to be wrong. But his attempts to evade the conclusions only led him into self-contradictions which, when exposed, produced the same effect upon the chemical mind that the reported insolvency of a great banking house produces on the financial world. The failure of a Berzelius shut up the current coin of theorising the world over.

(To be continued).

PROCEEDINGS OF SOCIETIES.

ROYAL INSTITUTION OF GREAT BRITAIN.
General Monthly Meeting, Monday, July 6, 1891.

Sir James Crichton-Browne, M.D., LL.D., F.R.S., Treasurer and Vice-President, in the Chair.

The following gentlemen were elected Members of the Royal Institution :—Messrs. Henry Claudius Ash, Henry T. C. Knox, and John George Mair-Rumley.

The special thanks of the Members were returned to Miss Jane Barnard, Dr. J. H. Gladstone, the Rev. A. R. Abbott, Mr. T. F. Deacon, Mr. A. Blaikley, and others, for the loan of the valuable and interesting collection of Faraday Memorials shown in the Library on the occasion of the two Lectures on June 17th and 26th given in commemoration of the Faraday Centenary.

The special thaaks of the Members were returned to Sir Frederick Abel, K.C.B., for his valuable present of an Oertling balance, and to Mr. Ludwig Mond for his donation of £100 towards expenses connected with the Faraday Centenary Commemoration.

The presents received since the last Meeting were laid on the table, and the thanks of the Members returned for the same.

NOTICES OF BOOKS.

Water Analysis : A Practical Treatise on the Examination of Potable Water. By J. Alfred Wanklyn and Ernest Theophron Chapman. Eighth Edition. By J. Alfred Wanklyn, M.R.C.S. London : Kegan Paul, Trench, Trübner, and Co., Limited. Small 8vo.

This manual has increased in size in its successive editions. The third edition, which appeared in 1874, numbered only 140 pp., whilst it now extends to 213 pp. But notwithstanding this enlargement the essential portion remains unaltered. The novel features of this edition are a chapter on specific gravity of drinking waters in connection with its purity or impurity. The author considers that " in extreme cases of well-contamination it might be desirable to take the specific gravity of the first small distillate yielded by a large quantity of the water." He very justly points out that this determination furnishes a check to the analysis. In these days it is difficult to say *à priori* what impurities may not be present in supposed potable waters, not to speak of river water and sewage. Mr. Wanklyn states that he in one case demonstrated the presence of benzol in a well water.

As a general rule he finds that the number of grains per gallon of total solids and of free carbonic acid approximately equals the number of centigrammes in excess of 1 kilo., which a litre of the water weighs. This seems to us a very useful result.

We find it stated that in many natural waters there is more carbonic acid in one state or other than " any other foreign material " taken singly. A considerable charge of carbonic acid in a natural water is laid down as a sign that the water has come from a considerable depth.

Mr. Wanklyn calls attention to the changes which waters undergo if kept for some time prior to analysis. The " free " ammonia decreases, and the " albuminoid " ammonia increases. Hence the interval between sampling and analysis becomes an important datum if different waters are to be compared.

The author's objection to magnesian salts in a water supply is perfectly justified.

A useful feature in this edition is the full account of

the "moist combustion process." As the patent for this process has expired, we hope that it will be widely tried and judged upon its merits.

On the value of the Wanklyn-Chapman process we shall not here make any remarks. We have expressed our opinion by occasion of the previous editions, and will now merely say that as the process has had twenty years' trial in nearly all civilised countries, it would have been abandoned before the present date if its results were unsatisfactory.

———

Piesse's Art of Perfumery and the Methods of Obtaining the Odours of Plants, the Growth and General Flower Farm System of Raising Fragrant Herbs. With Instructions for the Manufacture of Perfumes for the Handkerchief, Scented Powders, Odorous Vinegars and Salts, Snuff, Dentrifices, Cosmetics, Perfumed Soaps, &c. Edited by CHARLES H. PIESSE, F.I.C., M.R.C.S., &c. Fifth Edition. Published by Piesse and Lubin, 2, New Bond Street, London.

THIS work is something very much more than a treatise on the extraction and combination of perfumes. The author, in addition, treats his subject from the æsthetic and the biological point of view, and urges the development of the cultivation of the odoriferous plants in India and the colonies. He remarks in his preface that, "Of the five senses that of smelling is the least valued, and, as a consequence, it is the least tutored." This is unfortunately true. Yet as a means of scientific research smell comes second to sight alone, the place of hearing, except as a means of intercourse with our own species, being very low. In delicacy scent has been proved to exceed sight, even when the latter is aided by the spectroscope. Scent impressions, too, are so permanent that an odour once experienced and not met with again for half a lifetime is at once identified on its recurrence.

Mr. Piesse thinks he is justified in saying that "England now produces the finest perfumery in the world." Yet, as he shows, very much more might be done in this direction if the resources of India, Australia, South Africa, and the Antilles were duly brought into play. We are too apt to undervalue any manufacture unless, like the iron, cotton, or woollen trades, it gives scope for the investment of millions of capital and the employ of thousands of hands.

Some of our industrial rivals have kept in mind the old Scottish proverb, that "Many a pickle makes a mickle."

In the history of the art of perfumery, Mr. Piesse falls into one error. He writes:—"After the Romans had conquered Egypt, India, and Arabia." It is certain that they never conquered India and that their jurisdiction over Arabia never extended to those parts most likely to yield odours.

As regards the production and diffusion of odours, the author concludes that here, as in the cases of colours, sounds, and heat impressions, vibrations are the active agents. In a long quotation from the late Dr. Septimus Piesse, it is contended that the action of odours depends on the "force of volatility." He has even drawn up a table of "the degrees of volatility of odours, which indicates pretty nearly their relative strength." He points out that the essences obtained from flowers by distillation are not identical with the perfume exhaled by the living flower. He suggests that in the former case we may have to do with a hydrate of the original odoriferous matter.

He holds that there is an octave of colours like the octave of sounds in music. He asserts, with perfect truth, that there is a harmony and a discord of smells. Anyone who has met a ladies' school taking a "constitutional" will often have been unpleasantly struck with the discords given off when several successive damsels have been scented with odours which clash. The impression is as unpleasant as when we see scarlet and magenta grouped together in the same costume.

We find mention of two conditions of the olfactory organs in man mutually opposite, though both abnormal. Anosmia, a more or less complete deadness to scents—we want a word corresponding to deaf and blind—is far from uncommon. Hyperosmia is present in its highest degree in male moths of the genera *Saturnia,* &c., which can recognise the presence of a female of their species at distances exceeding a mile, though woods, houses, fences, and eminences may intervene.

The emission of odours by flowers is in many cases periodically intermittent. According to Warren, aromatic orchids become scentless half an hour after pollen has been applied. The night-blooming Cereus gives out jets of odour every half-hour. Odours are preferentially connected with certain colours. White flowers are the sweetest, whilst orange and brown flowers are apt to have disagreeable odours, the final cause of which is still a riddle.

It is a remarkable circumstance that offensive smells, where they occur, pervade the entire plant, as in the elder, the rue, wild garlic, &c. In sweet-smelling plants the fragrance is, with few exceptions, confined to the flower.

The animal kingdom is far richer in nauseous odours than in perfumes, as a visit to the Zoological Gardens may convince the sceptic. To the perfumer the animal world yields merely ambergris, castor, civet, musk, obtained from the musk-rat of Canada and the musk-deer of Central Asia. The quantity obtainable from the musk-beetle (*Aromia Moschata*) is far too small to render its collection remunerative.

As regards the practical information with which the bulk of the work is filled, it would not be fair to the owner to make extracts. We will merely say that it bears the stamp of a practical man, as distinguished from the compiler. Whoever wishes to undertake either the theoretical study of perfumes or their practical manufacture will find here most valuable indications.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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NOTE.—All degrees of temperature are Centigrade unless otherwise expressed

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Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxii., No. 26, June 29, 1891.

On the Persulphates.—M. Berthelot.—The author publishes his observations as they have been independently reproduced in Germany by Herr Moritz Traube, and put forward in support of a singular theory on a supposed neutral "sulphurylholoxide." The composition of barium persulphate, S_2O_8Ba, may be regarded as absolutely determined. This salt is soluble and neutral like barium permanganate, and may be separated by filtration from the accompanying barium sulphate. The persulphate is slowly decomposed in the cold into insoluble barium sulphate which is precipitated, oxygen which escapes, and sulphuric acid which remains free. There is no proof of the existence of a pretended neutral anhydrous compound such as the imaginary holoxide, SO_4.

Action of Sodium Alcoholates upon Camphor. New Method of Preparing the Alcoylcamphors.—M. A. Haller.—The author has studied the action of sodium ethylate, propylate, isobutylate, and amylate upon camphor, of sodium benzylate upon dextro-camphor, the properties of dextrobenzyl camphor obtained by means of sodium camphor and benzyl chloride, of dextrobenzyl camphor prepared by reduction, benzylcamphoroxime, lævobenzylcamphor, and dextro- and lævobenzylborneol.

On the Oxidation of Azo-compounds.— Charles Lauth.—The author finds that, in a general manner, on

submitting the azo-compounds to the action of various oxidising agents in the cold, the azo-group is split up, yielding, on the one hand, a diazo-compound, and on the other bodies of the quinonic series. Both alkaline and acid oxidising agents have been tried. Both give analogous results, but as the former promote the decomposition of the diazo-bodies they ought to be rejected. He adopts by preference lead binoxide in preference to sulphuric acid.

Moniteur Scientifique, Quesneville.
Series 4, Vol. iv., Part 2, No. 584.

Production of Cyanogen Compounds by Means of Atmospheric Nitrogen.—A. Breneman.—The author discusses the various conditions which have an influence upon the fixation of atmospheric nitrogen.

A Novel Method of Preparing Alkaline Nitrites.—G. A. Le Roy.—The author, after enumerating a number of methods already known (including a process of reduction by means of microbia discovered by Gayon and Petit) describes his own procedure. He causes 1 mol. BaS to react upon 4 mols. NaNO$_3$, obtaining thus the soluble nitrite and the insoluble barium sulphate. He mixes the two substances finely powdered, projects them by small portions into a cast-iron bowl previously heated to dull redness, and stirs the fused mass continually. The reaction takes place with effervescence ; the mass is taken up in water, which dissolves the nitrite ; the liquid is decanted, filtered, and concentrated to 35°—45° B. The barium sulphide employed must be free from carbon.

Rapid Process for the Preparation on the Large Scale of Silicon and Aluminium Chlorides and other Chlorides.—H. N. Warren.—From the *Chemical News* and the *Chemiker Zeitung.*

Sulphuretted Colouring Matters of the Primuline Group.—E. Trautmann.—This paper does not admit of useful abstraction.

Summary of Some Researches on Colouring Matters.—F. Reverdin.—This paper includes a notice of Flimms' synthesis of indigo by means of monobromoacetanilide and of Seidel's triphenedioxazine.

On Tannins.—Etti.—The author considers the extraction of tannins, the preparation of the phenylhydrazone of tannin ; the production of its oxime and the constitutional formula of the acetonic anhydride of gallic acid.

Distinction between Tannins Extracted with Alcohol and Those Extracted with Water.—Adrian. —From the *Bulletin de la Société Chimique.*

Use of Creosotic Acid in Tanning.—J. Hauff.—From the *Journal of the Soc. Chemical Industry.*

On Benzoyl Tannin.—Dr. Carl Böttinger.—If a dilute cold aqueous solution of tannin is treated with 5 c.c. of strong soda-lye, with the addition of benzoyl chloride, there is a reaction on stirring. The liquid at first turbid, becomes then dark, then red, and finally clear. A viscous matter is precipitated, which solidifies into small white globules. This mixture, on treatment with ether, gives a pastey mass. When taken up in water the substance hardens and yields ; when dried, a light yellow powder, insoluble in water, and boiling alcohol. It is soluble in aniline, dimethylaniline, phenylhydrazine, and slowly in hot soda-lye. The compound required is separated and purified by a tedious process.

MISCELLANEOUS.

The Durham College of Science, Newcastle-upon-Tyne.—Dr. Wm. C. Mackenzie has been appointed lecturer in Agricultural Chemistry in this College. Dr. Mackenzie was for four years assistant to Mr. Falconer King, of Edinburgh, in which capacity he gained great experience as an agricultural chemist in the analyses of manures, feeding-stuffs, &c. For three sessions he studied chemistry under Professor Crum-Brown at Edinburgh, obtaining the degree of B.Sc. and a number of medals and prizes. After this he studied a year under Professor Fittig, at Strassburg, and then obtained the degree of D.Sc. at Edinburgh, together with the Vaus Dunlop Scholarship of the value of £100 per annum for three years. At present he is working at agricultural chemistry as assistant to Professor Dr. Märcker, at Halle. Dr. Mackenzie will commence his duties in the College in September next.

THE CHEMICAL NEWS.

VOL. LXIV., No. 1652.

ON THE NATURE OF SOLUTION.
(No. II.)

By J. ALFRED WANKLYN and WILLIAM JOHNSTONE.

It has been shown that in the instance of cane-sugar there is neither expansion nor contraction when solution takes place, the volume of the solution of sugar being exactly equal to the volume of the sugar and the volume of the water forming the solution.

Starting with pure water, 100 c.c. of which weighs 100 grms., we may regard solutions of sugar as generated by the entrance of successive grms. of sugar into the 100 c.c., and the displacement of the corresponding quantity of water.

The increment of weight occasioned by the entrance of 1 grm. of sugar is given by the following formula:—

$$i_1 = 1 - \frac{1}{\text{sp. gr.}}$$

where i_1 equals the increment, and sp. gr. is the specific gravity of sugar.

It will be obvious that $\frac{1}{\text{sp. gr.}}$ is the weight of the water displaced by 1 grm. of sugar; and, as was shown in the former paper, the experimental result corresponded exactly with the theory. This may be conveniently symbolised by writing—

$$i = i_1,$$

where i equals the result of experiment, and is obtained by dividing the actual increment of gravity in a given instance by the number of grms. of sugar in the 100 c.c. of the solution of sugar.

It has already been shown that common salt behaves somewhat differently in the act of solution, and that in that case i is considerably greater than i_1. This we look upon is due to the circumstance that something besides solution takes place when salt dissolves in water. Picturing to ourselves the course of events, we see the gramme of salt entering the 100 c.c., but, instead of an *equal volume of water* being displaced and overflowing out of the vessel, there is chemical combination between salt and water and condensation, or absorption of part of the water.

This absorption is the difference between the value i and the value i_1, and $i - i_1 =$ the weight of the water condensed or absorbed when one grm. of a substance enters into 100 c.c. of solution.

Continuing the investigation we have experimented upon nitrates and sulphates as follows:—

Nitrates.

i.	i_1.	
0·696	0·553	$NaNO_3$.†
0·582	0·524	KNO_3.
0·639	0·470	$Ca(NO_3)_2$.
0·755	0·566	$Sr(NO_3)_2$.
0·782	0·686	$Ba(NO_3)_2$.
0·783	0·756	$AgNO_3$.
0·892	0·773	$Pb(NO_3)_2$.†

The only nitrate, so far as we have gone, which occasions little or no condensation of water on solution, is nitrate of silver. There is not much condensation in the case of the nitrate of potash, only 0·058 grm. of water being condensed by 1·000 grm. of that nitrate. The ratio is almost absolutely that of 18 : 303·3 or $H_2O : 3KNO_3$. The case of nitrate of soda is quite different—0·143 : 1·000 is the ratio, or $2H_2O : 3NaNO_3$. In the case of nitrate of strontia, the ratio is 0·189 to 1·000, being about—

$$2H_2O : Sr(NO_3)_2.$$
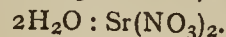
Sulphates.

i.	i_1.	
0·784	0·632	K_2OSO_3.
0·910	—	Na_2OSO_3.
0·974	—	$FeOSO_3$.
1·00	—	$CuOSO_3$.
0·89	—	$MgOSO_3$.

We defer our communications on these results until our next paper.

The Laboratory, 13, Fish Street Hill, E.C.
July 20, 1891.

MATTING THE SURFACE OF GLASS.

By NICHOLAUS S. NILSSON.

"WHITE ACID" is a name used by glass etchers to designate mixtures of hydrofluoric acid with various chemicals which are used for matting the surface of glass. The discovery of white acid is due to Berzelius, who, while engaged in his investigations on the properties of glass, made the discovery that fluoride of ammonium had the property of matting or opaquing glass. Since that time it has been found that other alkaline fluorides possessed the same power, and during the last few years this has been taken advantage of on a large scale for producing ornaments on glass of the greatest beauty. It is employed, principally, for producing ornamental figures on door lights, although it is used very extensively for decorating glass-ware for table use, and also for the various sorts of globes used on lamps and gas fixtures. Extremely fine effects may be obtained on mirrors, and the silvering may be placed on either the same or the opposite side from the etching.

During the last few years etching on glass has shown itself as a formidable rival to the sand-blast. the work generally being indistinguishable from that produced by the latter, except that acid is capable of producing effects of a much greater fineness and delicacy. The grinding is much more even, and therefore more easily cleaned.

In Germany, where the art has been carried to a much higher point of perfection than elsewhere, a number of formulæ for matt-etching are in use. Within a short time some of these have been published in various scientific journals, but they all belong to the category of what might be called slow acids, and are very unreliable and uncertain in their action, and possess very poor keeping qualities. They are made without the ammonia salt, and are dependent on soda and potash for their action, take a long time to work, and are too uncertain for practical use.

There is no doubt whatever but that the white acid, compounded with fluoride of ammonia, is the best. In using other white acids, spots and streaks often form in the glass, and these cannot always be removed by repeating the etching. With ammonia acids, however, any streaks which may appear, either from applying the acid unevenly or from imperfections in the glass, may be removed by repeated etchings. The following recipe is one which is used by several practical glass etchers, and is said to give good results. It is of German origin, and the only objection to it is that it is too complicated, which objection may also be raised to other recipes from the same source.

In a container of lead the following mixture is made:—

Distilled water	500 parts.
Fluoride of ammonium (strong) ..	500 „
Sulphate of ammonia	50 „
Sulphuric acid	100 „

This solution is ready for use within two hours, and may be tested by immersing a piece of clean glass, which should get a nice, fine, matt surface after five or six minutes.

In practical experience the writer has found that a simpler method of preparing the acid than the foregoing is capable of giving good results. Besides being cheaper, it is possible to recover the materials in it, should it for any reason get out of order.

A container of sufficient size is filled one-third full of ordinary commercial hydrofluoric acid. Carbonate of ammonia is then added. About equal parts by weight may be used. When effervescence has ceased, a small slip of clean glass is immerssd in the mixture, and permitted to remain six or eight minutes. Upon withdrawing it is rinsed in clean water, wiped, and dried. If examination shows that it has become evenly translucent over its entire surface, the mixture is all right and may be used for regular work. If, however, it is deeply and irregularly etched, with some parts clear and some parts ground, the acid is in excess, and carbonate should be added. If, on the other hand, the glass seems to be only partially affected by the acid, and, while being slightly ground all over, is transparent, too great an amount of ammonia has been used, and acid must be added.

With a little experience it is possible to keep the balance between the alkali and the acid, so that good results can be obtained. All white acids are subject to change in their actions from day to day, but in none of the recipes the writer has used can it be so easily regulated as in the foregoing. Before trusting any important work to the action of white acid, the acid should be tested with a clean piece of glass, and, by following the hints given, the acid can be corrected to give the proper action.

In preparing glass for etching any of the ordinary resists may be used. The drawing may be either put on glass by means of a ruling pen dipped in asphaltum properly diluted; by means of a brush; or by means of the somewhat antiquated process of covering the entire plate with Brunswick black and scraping away the parts which it is desired to grind. The best method, however, is that in which tinfoil is used, a description of which must be deferred to some future time. The design can also be transferred or photographed on glass if desired.—*Scientific American.*

ATOMICITY CUBES.

By J. BRAIK MASON, F.C.S.

TEACHERS of chemistry have found it somewhat difficult to get young students to grasp the facts of atomicity. This constantly recurring stumbling-block in the path of the learner led me to devise a simple mechanical contrivance, which has been found a great help in the way of imparting a better comprehension of things pertaining to the atom. There is usually found no particular hardship in grasping the nature of the atom itself—an ultimate particle, and therefore incapable of further subdivision. What offers the real hindrance to progress is the varying binding powers possessed by the different atoms. How to get a definite grasp of valency forms the difficulty.

To suggest a concrete assumption of what may be assumed as taking place, I take a number of square blocks of wood, painted white or different colours (or covered with paper), and proceed to liken one of these to an atom, explaining, of course, that an atom is so exceedingly small as to be incapable of being seen—an atom of any definite substance, as hydrogen, or oxygen, or sulphur. But, except that it may represent one atom of substance, it has no other character of its own. It does not represent a monad, or a dyad, or any other valency.

To give the atom a distinct monatomic character, a small screw, with hooked head, is inserted in one side, and this now represents a monatomic element, as H or Cl. Another similar hooked on then represents a molecule of H_2 or HCl. A dyad element, as oxygen, with its two bonds may be represented by a block with two screws, one opposite the other; and thus the molecule of water may be illustrated, the dyad bound to two monads. A block with three attachments for a triad, as P or Bi; and one with four hooks would represent a tetrad, as C or Si; and so on.

In this manner, by showing several examples of combination, taking representative compounds, I demonstrate what is generally admitted a difficult point, and succeed in producing in the minds of the youngest a conception of various atomicities that is readily grasped and accepted.

Laboratory, Y.M.C.A., Constitution Road, Dundee,
July, 1891.

CONTRIBUTIONS TO MICRO-CHEMICAL ANALYSIS.*

By H. BEHRENS.

(Continued from p. 32)

III.—*Lithium.*

1. With ammonium carbonate. Needles and prisms resembling crystals of gypsum and forming like the latter on the margin of the drop. They are slowly dissolved by water. Limit of the reaction at 0·00036 m.grms. Li.

2. With ammonium fluoride. This reaction, recently proposed by Carnot for the quantitative separation of lithium, produces mainly small colourless cubes, 15—25 micro.; immediately surrounding the ammonium fluoride there are rectangular dendrites up to 100 micro. The sensitiveness of the reaction is a little inferior to that of No. 1.

IV.—*Cæsium.*

1. With stannic chloride (Haushofer). Sharply developed, colourless octahedra of 30—40 micro., much less soluble in hydrochloric acid than the chlorostannates of potassium and rubidium. Limit of the reaction about 0·0016 m.grm. cæsium.

The liquid is evaporated to dryness and the residue dissolved in dilute hydrochloric acid before the stannic chloride is added. Salts of ammonia must be expelled by a strong heat after evaporation to dryness, as the ammonium chlorostannate is likewise very sparingly soluble in hydrochloric acid. Sometimes it is advantageous to convert the chlorostannate into the yellow iodo-chlorostannate by an addition of sodium iodide.

2. With ammonium silicomolybdate. Crystals like those of potassium phosphomolybdate, but much smaller, 2—6 micro. Limit of the reaction about 0·00025 m.grm. Cs.

As reagent there is used a saturated solution of ammonium silicomolybdate in water. It is not precipitated by salts of potassium, sodium, and lithium. Ammonium chloride precipitates rounded crystalline grains of 8—12 micro.; rubidium chloride yields similar granules of 8—20 micro.; thallium salts fall in still smaller granules than those of cæsium. The reaction succeeds best in solutions which contain a little free nitric acid.

Instead of silicomolybdate there may be used a saturated faintly acid solution of potassium platinum chloride or an acid solution of platinum chloride in 300 parts of water if evaporation is prevented. Concentrated solutions of cæsium are instantly precipitated in very fine crystals (3—5 micro.); rubidium falls afterwards in crystals three times larger.

V.—*Rubidium.*

1. With ammonium silicomolybdate. The crystals of rubidium silicomolybdate are distinguished from those of the cæsium compound just described merely by their

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* *Zeit. Anal. Chemie.*

size. They measure 10—20 micro. The limit of the reaction lies at 0·007 m.grm. rubidium; the limit of instantaneous precipitation is at the 100 fold dilution of rubidium chloride, whilst cæsium chloride is at once precipitated at a 300 fold dilution.

In order to detect rubidium in presence of cæsium the latter must be precipitated by an excess of stannic chloride in a strongly acidulated solution. After five minutes the clear liquid is drawn off and a little more stannic chloride is added. If after waiting for five minutes there is no further formation of octahedra, it is evaporated, ammonia is added, and after further evaporation and strong heating it is extracted with water. The clear extract is concentrated by evaporation, and tested for rubidium with ammonium silicomolybdate. Check experiments showed that traces of cæsium escape precipitation with stannic chloride.

2. The precipitation of rubidium with platinum chloride has been already mentioned when speaking of cæsium.

Precipitation with tartaric acid or sodium bitartrate cannot be recommended, as much potassium falls along with the rubidium.

VI.—*Thallium.*

1. With hydrochloric acid. From highly dilute solutions there are precipitated cubes of 10—15 micro.; from concentrated solutions cruciform rosettes of 50—100 micro. They are white by reflected light, but nearly black by transmitted light. Solubility 1 : 400. Limit of the reaction about 0·00016 m.grm. Tl.

Thallous chloride is rather easily soluble in hot water. From such a solution isolated cubes are always obtained. Sulphuric and nitric acids have also a solvent effect, and reduce the sensitiveness of the reaction.

2. With iodides. The same forms as under No. 1, but smaller. The rosettes measure at the utmost 20 micro. They are deep yellow and almost opaque. Solubility 1 : 4500. Limit of the reaction about 0·00003 m.grm. Tl.

3. With platinum chloride. Yellow octahedra, larger than those of cæsium-platinum chloride, which they otherwise much resemble. The reaction is exceedingly sensitive; its limit is about 0·000008 m.grm. Tl.

Phosphomolybdic acid gives very similar crystals. Alkalies convert the precipitate into thallous molybdate. (See Molybdenum).

VII.—*Silver.*

1. With chlorides and ammonia. Silver chloride dissolves in hot hydrochloric acid and crystallises from this solution in octahedra (Streng); it dissolves more readily in ammonia ((Haushofer), and crystallises on evaporation in cubes and combinations of $\infty O \infty$ and O. The crystals are definite but small (10—20 micro.), and refract light strongly. Limit of the reaction about 0·0001 m.grm. Ag. Chromates, phosphates, and arseniates have no influence. Gold chloride and platinum chloride produce dendritic structures of 50—90 micro. Mercuric chloride and ammonium molybdate interfere, and stannic chloride prevents the crystallisation.

2. With potassium bichromate. From solutions which contain *little* free nitric acid, the chromate, Ag_2CrO_4, separates out in large blood-red prismatic crystals, which may reach a length of 300, or even 2000, micro. The solution in ammonia does not yield good crystals. Large specimens may be much more readily obtained by repeatedly heating in the slightly acid mother-liquor. Limit of the reaction about 0·00015 m.grm. Ag.

VIII.—*Magnesium.*

1. With phosphor-salt and ammonia. Hemimorphous crystals of the rhombic system of 10—20 micro. From solutions containing more than 0·5 per cent Mg there are first deposited X-shaped skeletons and rudimentary crystals of the shape of letter-envelopes. Composition— $Mg.H_4N.PO_4 + 6H_2O$. Solubility 1 : 15000. Limit of the reaction 0·0000012 m.grm. Mg.

To the specimen drop there is added sufficient ammonia

and ammonium chloride; it is moderately heated and the precipitation is then effected by means of a granule of phosphorus salt. Application of heat, as proposed by Streng, much facilitates the formation of perfect crystals. It must be remembered that mixed crystals may be formed with the isomorphous double phosphates of ammonium and iron, manganese, cobalt, and nickel. Iron and manganese may be removed by waiting a couple of minutes between the addition of the ammonia and the phosphate. (See also Cobalt and nickel). It must be remembered that the reaction sometimes fails if the quantity of ammonium chloride is insufficient.

IX.—*Glucinum.*

1. With potassium oxalate. Massive crystals of a double oxalate which refract light strongly, of the form of natural crystals of gypsum, also swallow-tailed twin crystals, and forms produced by the coalescence of twins. Strong polarisation. Extinction below 40°. Size 100—200 micro. Limit of the reaction about 0·00008 m.grm. Limit of immediate precipitation at the 600 fold dilution of crystalline glucinum sulphate.

A small addition of potassium oxalate precipitates merely concentrated solutions of glucinum sulphate. There are formed X-shaped dendrites of an easily soluble oxalate. A moderate excess precipitates the double salt which has been already described and which is much less soluble. A large excess gives aggregates of pale lenticular rhombic crystals. Ammonium oxalate precipitates badly and sodium oxalate not at all. Ammoniacal solutions are to be evaporated to dryness, and the residue must be re-dissolved in hydrochloric acid. The solution must be neutral, and the potassium oxalate in excess.

With uranyl acetate and sodium acetate glucinum behaves like magnesium. (See Sodium).

(To be continued).

LONDON WATER SUPPLY.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, Metropolis Water Act, 1871.

London, July 6th, 1891.

SIR,—We submit herewith the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from June 1st to June 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 182 samples examined, the whole were found to be clear, bright, and efficiently filtered.

The water supplied to the Metropolis during the month of June, though not exhibiting that extreme degree of freedom from organic matter—present in small proportion

in potable waters generally — which characterised the supply for the previous month, maintained, however, the satisfactory character which the Metropolitan water has now presented continuously since the period immediately following on the breaking-up of the severe and exceedingly prolonged frost of last winter, the exceptional results afforded at that period being made a subject for comment in our report for the month of February.

During the past six months we have examined 1008 samples of the water distributed to the Metropolis by the companies drawing their supplies from the Thames and the Lea. The generally excellent quality of the water is shown in the abstract set forth in the following table of the results afforded by the Thames-derived supply during each of the consecutive six months respectively, the results afforded by the entire supply furnishing even yet lower figures.

	Ratio of brown to blue tint. Means.	Oxygen required for oxidation. Means.	Organic carbon per 100,000 Means.	Organic carbon per 100,000 Maxima.
January . ..	—	0·044	0·142	0·165
February. ..	—	0·081	0·263	0·489
March	14·1 : 20	0·049	0·146	0·209
April	13·9 : 20	0·055	0·155	0·190
May	9·6 : 20	0·042	0·136	0·150
June	14·4 : 20	0·060	0·153	0·181

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
WILLIAM ODLING.
C. MEYMOTT TIDY.

NOTE ON THE CALIBRATION OF BURETTES.

By DOUGLAS CARNEGIE, M.A.

THE method of calibrating burettes given in the text-books is roughly as follows :—

The burette is filled with water, and successive portions—corresponding to 5 c.c. or so—are run out into dry beakers. From the weights of these successive portions a table of corrections can easily be deduced. This method, in the case of an ordinary 50 c.c. burette and with 5 c.c. tests, involves at least eleven weighings and ten level-readings.

The method of calibration I would suggest is, I believe, more accurate than the above, and involves no weighing whatever ; for it is quite a matter of indifference to the chemist, whose measurements are all relative, whether he adopts as his unit the true cubic centimetre or an arbitrary one.

The principle of the method consists in causing a constant volume of liquid to slide in the burette (so that it may be made to assume any desired position therein), and then reading off its length in terms of the burette divisions.

In fig. 1 the burette, B, is attached by means of caoutchouc tubing, C, to a reservoir, R, which is filled with water, and which can easily be raised or lowered by sliding the clamp K along S. On the surface of the water in the burette there is a small column of carbon bisulphide, W, which obviously can be made to assume any desired position in the burette by either raising or lowering R, and then turning the stopcock, n, very gently.

In my first experiments I used mercury in place of water in R, and water instead of carbon bisulphide as a movable index. But this combination was unsatisfactory ; I found it exceedingly difficult to read the level, l, both on on account of the convexity of the mercury surface and also on account of the peculiarly disturbing light reflection from the bounding water-mercury surface.

The combination, water and CS_2, works admirably if the following precautions be taken :—
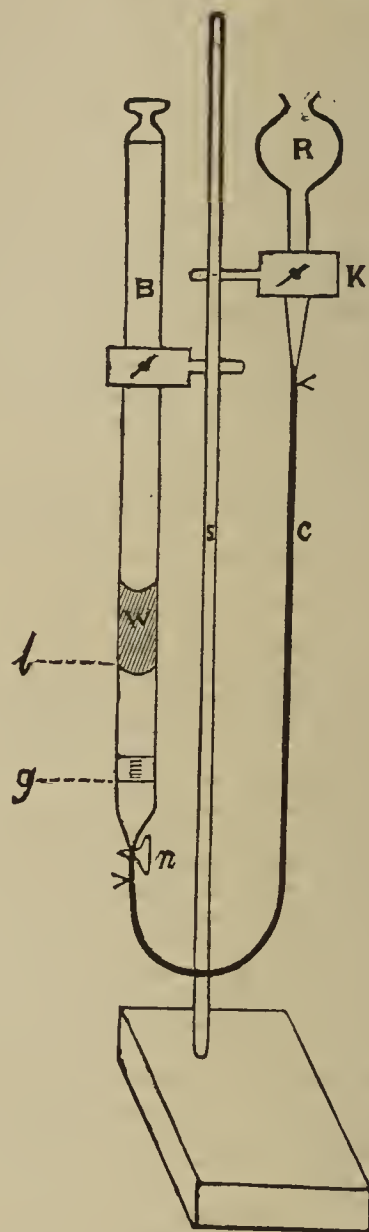
FIG. 1.

The burette must be *thoroughly cleaned* from grease and dust before calibration. The reservoir, R, is then filled with freshly distilled water, and matters are so arranged that the level of the water stands at g, the *lowest* graduation of the burette. A long thistle funnel is then inserted into the burette, and a small quantity (say
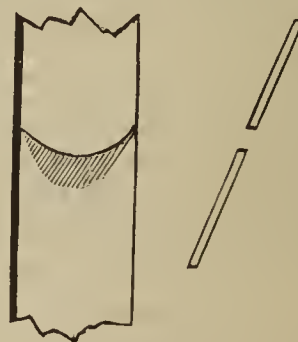
FIG. 2.

5 c.c.) of recently distilled CS_2 is poured gently on the surface of the water . Under these circumstances the CS_2, in spite of its higher specific gravity, floats on the water, and exhibits two easily localised concave meniscuses. It is well to shake the CS_2 up with distilled

water so as to thoroughly saturate it, and to tint it slightly with iodine before pouring it into the burette.

The method of procedure is obvious. I will merely add that, in altering the position of the CS_2 index, it is well to let it rise a little higher in the burette than the required graduation, and then lower it by careful manipulation of the stopcock, *n*. The burette should of course be kept stoppered as much as possible during the calibration.

I would also particularly emphasize the fact that the method works satisfactorily *only* when the calibration is effected as described—from below upwards.

The readings obtained can be used for calibration as described in detail in Bunsen's " Gasometry."

In order to avoid errors of parallax in reading off the levels of the CS_2 column, I silver a strip on the back of the burette. This mirror strip, which does away with all floats and similar devices for avoiding errors of parallax in the subsequent use of the burette, is easily made as follows :—The burette, having been thoroughly cleaned externally, is corked air-tight, and then inverted in a tall cylinder containing an alkaline silvering fluid.* After some time it is withdrawn, and allowed to become *thoroughly air-dried.* The silver can then be easily removed from the front and sides by scraping, followed by a final rubbing with a rag moistened with dilute nitric acid. The strip of silver backing the burette is then fixed by one or two coats of varnish.

In reading such a burette it will be found advantageous to look at the meniscus through a slit cut in a sheet of white glazed paper, held at an angle to the vertical as shown in fig. 2. The burette graduations are also rendered very much more distinct by rubbing the front of the burette first with a piece of flannel on which a paste of turpentine and mercuric iodide has been placed, and then with a dry cloth.

NOTES ON
CARBON IN " EXPERIMENTAL STANDARD."

By P. W. SHIMER.

My first results on the " Experimental Standard " distributed by Prof. J. W. Langley among the members of the American Committee on International Standards of Iron and Steel, were 1·055 per cent carbon in the sample marked "Ingot," and 1·052 carbon in the sample marked " Hammered." These results were obtained by use of double chloride of copper and ammonium solutions and combustion in a porcelain tube with the usual purifying apparatus, including anhydrous copper sulphate tube. These determinations were made before it was known that the double chloride usually contains carbonaceous matter. The copper solution was made as nearly neutral as possible before using.

After Dr. Dudley had shown that the results obtained by use of the double chloride of copper and ammonium could be varied by varying the method of making the double chloride, I endeavoured to determine the absolute total carbon by direct combustion of the steel in a current of oxygen. Owing to the length of time required to make a direct combustion in a porcelain tube (four to six hours) these efforts were not successful. The combustions were made on the " Ingot," reduced by grinding until part of the sample passed through a 35-mesh sieve. This fine material was then burned in oxygen in a porcelain tube. In some of the experiments the steel was intimately mixed with coarsely crushed Fe_2O_3 previously ignited to constant weight in oxygen. In other experiments CuO was used in place of Fe_2O_3. In still other cases, a long copper boat, previously ignited to constant weight in oxygen, was used. The powdered steel was evenly and

thinly spread on the bottom of the boat, which the ignition had covered with a coating of CuO. The results of six combustions were — 1·072, 1·058, 1·077, 1·065, 1·076, 1·072. These results were not worthy of confidence, because of the strain upon the constant weight of the potash bulbs by reason of the long combustion of four to six hours. Suspecting that the oxygen might contain a trace of carburetted gas not absorbed by KOH solution, I placed a second porcelain tube containing CuO directly above the combustion tube in the furnace. On making a combustion, the oxygen was first passed through the upper tube, then through KOH, then into $CaCl_2$ tube and combustion tube. In this way a good constant weight could be maintained for long combustions. By this arrangement a direct combustion, requiring five hours, gave 1·047 per cent carbon in the " Ingot."

If the double chloride of copper and ammonium contains carbonaceous matter it occurred to me that it might perhaps be removed by filtration of the solution through charcoal. For this purpose a glass tube, 27 inches long, was filled with crushed charcoal, and the copper solution was slowly filtered through it, being finally passed through ignited asbestos to remove minutely divided carbon in suspension. Samples of 3 grms. each of the " Ingot " were dissolved in 200 c.c. of the above filtered copper solution previously made acid by addition of 10 c.c. HCl, sp. gr. 1·12. The results were 1·036, 1·034.

The original copper solution, without filtration through charcoal, was then used in the same way. The result was 1·040. This difference is not large enough to have any decisive significance. But it will be worth while to try the effect of filtration through charcoal upon a more impure sample of the double chloride than mine happened to be.

I next tried the double chloride of copper and potassium as a solvent in the manner recommended by Mr. Blair. The results were 1·036, 1·038.

After the solution of the steel in the above five determinations, the carbon residues were filtered upon ignited asbestos (without use of suction) in Dr. Drown's wide-necked carbon funnels. (*Journ. of Anal. and Applied Chem.*, ii., 330.)

When the carbon was all in the funnel, the asbestos was liberally soaked with cold HCl, sp. gr. 1·12, and allowed to remain in this condition for a few minutes, in order that all chlorides might be rendered easily soluble. The carbon was then washed (without suction) with hot water, twenty to thirty times, until the filtrate showed no chlorine by silver nitrate. After drying at 90° C., the carbons were transferred to the porcelain combustion tube, which contained nothing but the usual CuO. The apparatus was put together in the following order :— 1. Oxygen tank ; 2. Porcelain tube containing CuO, placed immediately above the combustion tube in the furnace ; 3. KOH bulbs ; 4. $CaCl_2$ tube ; 5. Combustion tube containing CuO ; 6. A Liebig potash bulb, containing nothing but a drop of water in each of its five bulbs, and cooled by filter-paper kept wet by dipping in cold water; 7. $CaCl_2$ tube ; 8. KOH bulbs, with the usual $CaCl_2$ tube attached ; 9. A guard of $CaCl_2$. After completing the above five combustions, the few drops of water were removed from the Liebig bulbs, and found to contain no chlorine when tested by silver nitrate. Evidently the method of washing the carbon residue (by liberal treatment with HCl and thorough washing without suction) has removed all chlorides, for any hydrochloric acid or chlorine escaping from the combustion tube would be condensed or absorbed in the cold and moist Liebig bulbs. I cannot help thinking that a too sparing use of HCl on the carbon residue, and a too rapid washing by suction, is responsible for much of the trouble with hydrochloric acid and chlorine. In order that wash-water may thoroughly dissolve impurities, it must be given time to act upon them. From the fact that the results obtained as detailed agree so closely with the results obtained in the admirable apparatus devised by Mr. Blair, I am

* Suitable fluids are described in Roscoe and Schorlemmer's ' Treatise on Chemistry ' vol. ii., part 1, p. 363

still further encouraged to believe that the HCl difficulty may perhaps be overcome at its source by washing in the manner described, and, as a further precaution, by the use of some simple condensing and absorbing arrangement, like the moistened Liebig bulbs. More experiments, however, be made to decide these points.—*Journal of Analytical and Applied Chemistry*, vol. v., p. 129.

THE DECOMPOSITION OF CHROMITE BY THE ELECTRIC CURRENT.

By EDGAR F. SMITH.

Two years ago I mentioned[*] that if finely divided chromite were suspended in melted alkali, and an electric current allowed to act upon the mixture, the mineral would undergo decomposition, its chromic oxide being changed to a soluble alkaline chromate. Details of the experiments made at that time were not published, because difficulties were encountered which necessitated a more careful study of the subject.

The early trials were made with a current of 1 ampère. The oxidation of the mineral was apparently finished in fifteen minutes, but the desire to reduce the time factor, by increasing the strength of the acting current, led me astray. Many successful and unsuccessful decompositions were made before conditions were found which gave satisfactory results. Among other things it was observed that by using a strong current the latter seemed to act chiefly upon the iron oxide and the caustic alkali, liberating larger or smaller quantities of the metal from each. After the decomposition of the mineral had proceeded to a certain extent, the action just mentioned seemed to commence, and undecomposed chromite always remained. Without describing the various modifications that were tried in the hope of obtaining success, I will briefly outline the method which finally gave, and has continued to give, good results.

Method of Oxidation.—Melt 30 to 40 grms. of stick potash in a nickel crucible, $1\frac{7}{8}$ inches high and 2 inches wide; heat gently until the excess of moisture has been expelled. The crucible is then placed upon a heavy copper-wire ring, attached to the anode of a storage-cell.[†] A small flame is held under the crucible during the entire decomposition. The weighed mineral is carefully brushed from a watch-crystal upon the liquid alkali, the crucible covered with a perforated glass, and the platinum rod, attached to the cathode of the battery, lowered into the melted mass. Set the current in operation; particles of the melted material are thrown against the under-side of the cover-glass, but the liquid soon collects in drops and falls back into the crucible, thus returning any traces of ore that at first may have been projected from the crucible by the bursting of the gas-bubbles.

Experience has demonstrated that it is best to make the crucible the anode; but, before finally interrupting the current, the latter should be reversed by means of a commutator, which, together with an ampèremeter, is always in circuit. The current is reversed for this reason:—metallic iron is deposited upon the cathode and may enclose particles of the ore, removing them from the oxidising field. By reversing the current the imprisoned material is set free and exposed to oxidation.

The quantity of mineral taken for a determination may vary from 0·1 to 0·5 grm. It should be quite fine, although it was never as finely divided as seemed necessary for complete decomposition by other methods. The current employed in the oxidation of the material *should not exceed one ampère* for the quantities given above. As to the time required for the decomposition, it can only be

said that while the greater part of the mineral is unquestionably decomposed in fifteen minutes, it is best to let the current act for a period of thirty to forty minutes. Much depends upon how refractory the sample under analysis may prove to be. Chromites vary in this respect. It is a difficulty with which all methods must contend. Hence at least one half-hour should be allowed for an oxidation by the electrolytic method. As the decomposition advances the melted alkali acquires a yellow colour. The portion that creeps to the edge of the crucible and about the cover-glass has the appearance of cauliflower.

The current can now be interrupted. Raise the platinum rod (the cathode) from the liquid, remove the cover-glass carefully from the crucible with a nickel tongs, rinse its under surface with water, collecting the latter in a beaker. The crucible is lifted from the ring supporting it, and allowed to cool. The platinum cathode should be rinsed with water. It will show a black appearance, due to the metallic iron that had been deposited upon it. It is my plan to dissolve off the iron with dilute hydrochloric acid, to assure myself that undecomposed ore was not present.

When the nickel crucible is cold, place it in a beaker of 300 c.c. capacity, cover with water, and digest upon a warm iron plate. In a few minutes the contents of the crucible can be entirely removed. The liquid now contains the excess of alkali, sodium aluminate, silicate, manganate, chromate, &c. After digesting for some time upon a warm iron plate, filter off the insoluble portion and thoroughly wash it with boiling water. The yellow alkaline solution is now ready for the determination of the chromium.

Treat the residue with warm hydrochloric acid. It should dissolve. It may happen that when quartz is present in the ore there will be a slight residue; but this is immaterial, provided it is not dark in colour. In the analyses given later, the oxides remaining after treating the fused mass with water *dissolved completely* in warm hydrochloric acid.

Chromium Determination.—This may be made either gravimetrically or volumetrically. In the latter determinations I used the volumetric method almost exclusively. To this end the chromate solution was acidulated with sulphuric acid, and a weighed portion of ferrous sulphate added, the excess being determined with a standardised bichromate solution. Potassium ferricyanide served as an indicator. In several instances the excess of ferrous salt was determined with potassium permanganate. This course, however, was abandoned, as I failed to read the end reaction with sufficient accuracy. By using the volumetric method I believe it possible for the analyst to decompose a chrome ore and determine the chromium content within the space of an hour. Several crucibles can be connected up in the same circuit, and a series of determinations made quite rapidly and with as much accuracy as by any one of our present methods.

Results.

1. 0·1080 grm. chromite gave 51·77 per cent Cr_2O_3.
2. 0·4787 grm. chromite gave 51·55 per cent Cr_2O_3.
3. 0·2729 grm. chromite gave 51·23 per cent Cr_2O_3.
4. 0·1085 grm. chromite gave 51·74 per cent Cr_2O_3.
5. 0·4184 grm. chromite gave 52·02 per cent Cr_2O_3.

By the Dittmar method of decomposition a sample of the same ore gave 51·70 per cent Cr_2O_3.

A second chromite, decomposed by the current, gave as follows:—

6. 0·1515 grm. chromite gave 48·01 per cent Cr_2O_3.
7. 0·2029 grm. chromite gave 48·34 per cent Cr_2O_3.
8. 0·3174 grm. chromite gave 48·21 per cent Cr_2O_3.
9. 0·2071 grm. chromite gave 48·38 per cent Cr_2O_3.

A portion of the ore oxidised by the Genth method and the chromic oxide determined gravimetrically gave 48·50 per cent Cr_2O_3.

* *J. Franklin Inst.*, April, 1889; *Ber. d. Chem. Ges.*, xxii., 1019.
† A picture of the apparatus arranged for a decomposition of this kind is given in *Ber. d. Chem. Ges.*, xxiii., 2276; *J. Franklin Inst.*, cxxx., 145; and in the writer's "Electro-chemical Analysis," p. 111.

A light-coloured chromite powder gave the following results :—

10. 0·2012 grm. chromite gave 32·00 per cent Cr_2O_3.
11. 0·2130 grm. chromite gave 31·50 per cent Cr_2O_3.

A gravimetric determination of the chromium, after decomposition by the method of Dr. Genth, gave 31·90 per cent Cr_2O_3.

A fourth specimen of chromite showed the following percentage of chromic oxide, after decomposition by the current :—

12. 0·2295 grm. chromite gave 42·20 per cent Cr_2O_3.
13. 0·2225 grm. chromite gave 41·70 per cent Cr_2O_3.

By the Genth method this ore gave 41·30 per cent Cr_2O_3, while 41·98 per cent Cr_2O_3 was found after a decomposition made by the Dittmar method.

The writer would here acknowledge his indebtedness to Mr. D. C. Wallace for the care and skill with which he conducted the many oxidations that were considered desirable before publishing the facts contained in this communication. — *American Chemical Journal*, vol. xiii., p. 414.

GASOMETRIC DETERMINATION OF OXYGEN IN GASEOUS MIXTURES.

By L. L. DE KONINCK.

THE number of reagents proposed for this purpose is very considerable. Winkler mentions especially hydrogen, phosphorus, the alkaline metals, copper either raised to a high temperature or moistened with hydrochloric acid or ammonia, lead or even thallium in moistened shavings, nitric oxide in the state of gas or dissolved in ferrous sulphate, calcium sulphide, ammoniacal copper chloride, ferrous hydrate recently precipitated (ferrous sulphate and potassium hydrate), sodium hydrosulphite, the alkaline pyrogallates, and white indigo ; to which we may add chromous chloride, as proposed by Von der Pfordten.

Most of these substances are, from one or other cause, open to objections. Potassium pyrogallate is the substance most frequently in use, at least for industrial determinations.

But this reagent leaves something to be desired in several respects. As regards exactitude it has the defect of sometimes occasioning the formation of a small quantity of carbon monoxide. It is further extremely alkaline, staining strongly whatever it touches, which renders its use with Bunte's burette disagreeable ; and, lastly, its price is very high.

To avoid these different inconveniences we have endeavoured to return to the use of metallic solutions.

We first tried the ferrous salts. The oxidisability of these salts in neutral or acid solutions is so feeble that they do not absorb oxygen completely in a relatively short time. It was necessary to employ them in an alkaline solution, but the addition of alkali produces a permanent precipitate, and the oxidisable matter (the ferrous hydrate formed), being in suspension in the aqueous liquid, does not come in intimate contact with the oxygen to be absorbed.

In order to obtain the ferrous salt in an alkaline solution we had recourse to the tartrates. The reagent was obtained by mixing the following solutions in the proportions given below :—

A. 40 grms. crystalline ferrous sulphate.
B. 30 grms. double potassium-sodium tartrate (known as Seignette's salt or Rochelle salt).
C. 60 grms. commercial potassium hydrate.

Each substance is dissolved in the quantity of water necessary to make up 100 c.c. of solution.

One volume of A is passed into 5 vols. of B ; there is formed an abundant whitish precipitate of ferrous tartrate, which disappears on the immediate addition of 1 vol. of C to the solution.

We obtain thus a light yellowish solution, which, if exposed to the air, turns green in consequence of the formation of a ferroso-ferric salt, whilst a perfectly ferric salt is also clear.

The order in which the solutions are mixed is not indifferent. If we first mix the potassa and the double tartrate, and then add the ferrous solution, we do not obtain a clear liquid.

The proportions given above have been reached after some trials, from which it appeared that too small a proportion of tartrate produces a dark, or even a turbid, solution. When the proportion of tartrate is sufficient an excess of alkali does not modify the appearance of the liquid.

If used in a double Hempel's pipette for the analysis of air, by means of the Hempel-Winkler burette, graduated in fifths of a c.c., the results showed, as the mean of four determinations, 21·0 per cent of oxygen.

If the pipette is agitated, the rapidity of absorption is very satisfactory ; in our experiments the oxygen (in samples of atmospheric air) was completely absorbed in four minutes.

The trials hitherto made with stannous chloride have not given satisfactory results ; like the ferrous salts, stannous chloride can only be employed in an alkaline solution.—*Revue des Mines*.

INSPECTION OF CHEMICAL WORKS.

IN the discussion on the Local Government Board Vote, in the House of Commons, on Wednesday, July 15th, Mr. BRUNNER, M.P. for Northwich, said :—" Then there is another matter which I think comes under this vote,—the Inspector of Alkali Works. The law at present is in a very anomalous condition. There are a number of manufactories in the country where the business comes under the designation of Alkali Works. These works carry on operations on a large scale, and are prevented, under the Act, from the discharge of noxious vapours ; but, strange to say, in other works, where they use the products made in the larger manufactories, the Act does not apply. In point of fact there are smaller factories using the products of the larger works, and discharging fumes which do quite as much mischief as those which are evolved from alkali works. Oddly enough, if the Inspector can induce the owners of these works to consume these noxious gases instead of turning them out into the air, then the works come under the Act. Those who carry on their work in the most wasteful and harmful fashion are not watched ; but as soon as a man ceases doing mischief to his neighbours, then he comes under the watchful eye of the Local Government Board Inspector. If the Right Hon. gentleman (Mr. Ritchie) will consult with the officials of his Department, he will, I have no doubt, find that they are entirely at one with me in this matter, and he may be assured an amendment of the law will have the hearty co-operation of the manufacturers who do come under the Act. So far as the sanitary authorities who understand this matter—more especially in London, where the mischief is rife—are concerned, he may rely upon their support too. I hope the Right Honourable gentleman (Mr. Ritchie) will consider the representation made to him on this subject, and endeavour to put the law into a condition consistent with common sense."

Mr. RITCHIE—" I have to say that the matter has been under our consideration, and a Bill to amend the Alkali Acts has been prepared, and I believe it would meet the views of the honourable gentleman ; but there has been no opportunity of introducing it this session. I hope the Alkali Acts will be so extended as to embrace the offending factories mentioned by the honourable member, with regard to which I am quite at one with him."

THE PROGRESS OF CHEMICAL THEORY: ITS HELPS AND HINDRANCES.*

By Dr. PERSIFOR FRAZER, Prof. of Chemistry.

(Concluded from p. 36).

BERZELIUS believed that the radicles were unchangeable. Liebig and Dumas were not convinced of their entire unchangeability. The two sets of views separated more and more. Liebig finally defined a radicle as one which must me (1) an unchangeable unit in a number of compounds ; (2) it must be replaceable in these by simple bodies ; (3) it must allow the simple bodies with which it is combined to be replaced by others to form with it new compounds. This was the old radicle theory.

In 1827, J. B. Dumas (1800—1884) commenced a series of researches on the vapour densities of many substances which are solid or liquid at ordinary temperatures, and showed that if Gay-Lussac's law of the identity of atom-weight with gas-volume-weight be true, then some of Berzelius's atom-weights were double and some were half what they should be. This cast doubt on the truth of the law as well as on Berzelius's work, but the latter held fast to his numbers (which were right), and simply confined his employment of the volume theory to permanent gases. The effect upon the minds of chemists, however, was disastrous ; for even Gay-Lussac, Liebig, and others despaired of getting any information as to the atoms, and fell back on the equivalents which were shortly afterwards more precisely defined by Faraday as the contemporaneous quantities of the various constituents of compounds which an electric current of given intensity would disengage. This he called the law of constant electrolytic action.

Under the unfortunate fear of having been misled, all attempts at theory were suspended. Gmelin, in the colossal work which bears his name, went back to the apparent weights of combination of Lavoisier's time, and the soul was taken out of the science. But Dumas dealt Berzelius a heavier blow still in the field of organic chemistry in his substitution theory, which he called " metalepsie," of which the two propositions were :—

1. If a hydrogen compound is subjected to the action of chlorine, iodine, or bromine, it takes for every atom of hydrogen lost an atom of one of these elements to replace it.

2. If the body contain water, it loses this without replacement.

Auguste Laurent (1807—1853) went further and asserted that the congeries of atoms called radicles which had suffered this substitution of H by Cl, or the loss of water, remained practically the same in properties. This was called the nucleal theory, which was short-lived, but before it had quite disappeared from the field, Dumas came forward with his discovery of chloracetic acid, and declared himself for Laurent.

He maintained that the newly-formed body in such substitutions must resemble the old, and he classed such original and substituted products together as derivable from the same type. This is called the old-type theory to distinguish it from the new-type theory subsequently set up by Laurent and Gerhardt. Dumas showed that his trichloracetic acid, in spite of the substitution of six atoms of chlorine for six atoms of hydrogen, was similar in its behaviour and characteristics. He stated that " in organic chemistry there are certain types which remain constant even when one substitutes an equal volume of Cl, I, and Br for their H." Acetic and trichloracetic acid, aldehyd and chloral, marsh gas and chloroform, belong to the same chemical type. He went so far as to assert that all bodies derived from each other by equivalent substitutions belonged to the same "mechanical type." This was followed by the following declaration

of war against Berzelius's dualistic theory. " Every chemical compound forms a complete whole, and does not consist of two parts. Its chemical character depends principally upon the number and arrangement of its atoms, and secondarily upon their chemical nature."

Berzelius was obliged to account for the facts discovered and to conform his explanation to the new discovery of Melsens in 1842, that chloracetic acid was reduced to acetic acid by potassium amalgam. He finally decided to do this by supposing that—

$$C_2(H_2)_3 + C_2O_3 \cdot H_2O = \text{acetic acid.}$$
$$C_2(Cl_2)_3 + C_2O_3 \cdot H_2O = \text{chloracetic acid.}$$
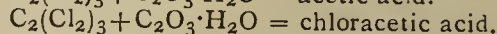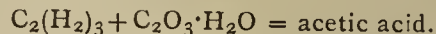
In other words that acetic acid consisted of a radicle (C_2H_6), and trichloracetic acid of the corresponding radicle (C_2Cl_6), each respectively paired with oxalic acid ($C_2O_3 \cdot H_2O$).

But in doing this he gave up the very principle that he had been contending for, viz., that the radicles were unalterable, since it was evident that in the first two symbols of the formulæ a radicle C_2H_6 had been changed by substitution into C_2Cl_6.

This admission weakened the faith of his most admiring followers, and threw the blight of timidity over the speculations of chemists for thirty years. And yet withal, Berzelius was right in almost every important generalisation which he made, and right (within the resources of his time) in every constant he established. Chemistry without his contributions would yet be a mere scaffolding.

The history of this controversy, the most important which has taken place since the commencement of the modern science, is useful as an illustration of another kind of hindrance to the progress of intelligent theory. It is a too-blind devotion to one man, and despair of attaining the object which he strove for if he has failed. It is true that if ever hero worship were justifiable, that of Berzelius was, but to sweep aside the whole fabric of his labours because part of his theory was proved untenable was the veriest cowardice and injustice to him.

How many a chemist in the last forty-five years has struggled through a jungle thick planted with the pretty crotchets of mediocre men, wondering what all this jargon meant and whither it was tending ; deprived of the vivifying influence of a high and noble thought, and condemned to delve and grub without reasoning, because one of the greatest geniuses of original research the world has ever seen was worsted in an encounter on a small part of his field, and a part to which he had not devoted the best of his thought !

Among the most innocent looking hindrances to the development of sound chemical theory must be reckoned an hypothesis which was given anonymously to the world in 1815, and which was later referred to its true author, Dr. Prout. This was the supposition that the atomic weights of all elements were even multiples of that of hydrogen.*

No argument was offered to show why this should be true, but it had the specious and enticing appearance which captivates that sense of order which is a human instinct.

Prout did not hesitate to add the obvious conclusion that hydrogen was the original material, or as one of the greatest of living chemists has put it, the protyle.

By the usual rule which exists in such cases, Prout should not have had credit for anything more than a pretty idea, which, besides, was only a modification of a similar thought of Thomson, the collaborator of Dalton, who believed that the atomic weights of the elements were multiples of that of oxygen. Prout was more nearly right, of course, because the weight of hydrogen is only about one-sixteenth as great as that of oxygen, and is a more general divisor. But in spite of all, this pretty thought strongly influenced many admirable chemists,

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* Introduction to the Chemical Lecture Course at the Franklin Institute, November 10, 1890.

* It should be stated that Profs. Crookes, F. W. Clarke, and other chemists of the first rank still show a leaning towards the acceptance of something lide Prout's " law."

even those like Dumas and Stas and Marchand and Erdmann, whose labours in accurately determining atomic weights did more than all else to prove the baselessness of Prout's assumption.

Even to-day the tendency is manifested to get back to the even numbers which Leopold Gmelin adopted in his great work, in entire disregard of the accurate results of Berzelius. It must be added that some are prevented from falling into this snare through the hope that the real protyle will be some day discovered, and that being lighter than hydrogen it will provide a table of atomic weights less disfigured by fractions than the present one.

The moral of this theory is that healthy scientific work must not be influenced by premature attempts to put a finish on it and make it appear symmetrical.

The discovery of an element lighter than hydrogen and possessing properties which, as it will be seen, we can to a certain degree predict, might render very desirable those ugly decimal affixes to the present atomic weights in order to show that experiment supported theory. On the whole, Prout's "law," as it is called, is a hindrance, and quite an annoying one.

The downfall of dualism and the establishment of unitism in compounds was followed by a storm of conflicting notions of chemical union, into all of which it is not necessary to enter.

To Laurent and Gerhardt is due the praise for unifying in the new theory of types the opinions which had been previously thought to be diametrically opposite. It has been said that the uncertainty which prevailed upon the overthrow of the dualistic theory of Berzelius caused most chemists to go back to the old equivalent weights $O = 8$, but Gerhardt opposed this weakness and strongly maintained the correctness of the numbers of Berzelius, merely correcting his early atomic weights for the alkaline metals in conformity with the then acquired knowledge of the existence of two atoms of the metal in the alkalies. He showed that the quantities of H_2O, CO_2, &c., separated in the reactions of organic compounds did not represent one equivalent each, but two. His aim was to reduce all formulæ to one criterion, which in the case of gaseous substances, was two volumes. His view was, that when two bodies react, one constituent of one (H), uniting with one constituent of the other (O), leaves two residues which unite. Hofmann discovered the substitution products of ammonia and thus established the ammonia type. Williamson established the water type and referred alcohols, ethers, acids, bases, and salts to this type. Gerhardt recognised the hydrogen type, the water type, and the ammonia type, but considered the compounds under them units and not couples.* Laurent explained the atom as the least part of matter that can take part in chemical combination; the molecule as the least part which can exist alone, and the equivalent of elements as those quantities which would perform the same amount of chemical work.

Thus the new type theory was a compromise skilfully constructed to save the Berzelians from chagrin while embodying all of value in their system. It took the idea of type from Dumas, that of radicle from Berzelius, but with the difference that it did not presuppose the groups of atoms called radicles to be necessarily capable of existing alone. Gerhardt admitted that the elements substituted in radicles did change the character of the compound.

Kekulé, in the year of Gerhardt's death (1857), added the conception of mixed types.

It is unnecessary to pursue this branch of the theory farther. An entirely new discovery appeared which was

* Dr. Wolcott Gibbs, in 1858, after referring to his attribution of the theory of water types to Gerhardt and Williamson, says: " I have not done justice to T. Sterry Hunt, to whom is exclusively due the credit of having first applied the theory to the so-called oxygen acids and the anhydrides; and in whose earlier papers may be found the germs of most of the ideas on classification usually attributed to Gerhardt and his disciples."—*Chem. and Geol. Essays*, p. 468.

a welcome light and enabled many of the obstacles in the way of progress to be seen and surmounted.

Frankland, after an investigation of the alcohol radicles, first announced his views of valence in 1853.

Kolbe, in 1855, accepted his thory and declared that the fatty acids, if imagined free of water, were derivatives of CO_2 or C_2O_4 in which one atom of oxygen is replaced by C_2H_3.

Frankland's discovery was really a corollary of multiple proportions, and had been vaguely foreshadowed by Wöhler, who said that one atom of antimony was equal to three of hydrogen.*

It is simply, as Hofmann expresses it, chemical value in exchange. Some elements, of which H is a type, can only combine one atom to one atom; some, like oxygen, can hold two atoms of the first-named kind in union. Some, like nitrogen, can hold three, and some, like carbon, four. Kekulé, in 1858, determined this valence of carbon, added another to the list of types which led to the establishment of the ring structure of some organic compounds.

Erlenmeyer found that every element had a highest valence, but might not use all of its combining powers. Wurtz and Naquet believed the valence changeable, Kekulé believed it fixed, and that only compounds using all the valences of every constituent were real chemical compounds. It appears to be the general opinion now-a-days that the valence of elements is not only variable, but that it does not even vary, as was supposed, by the suppression of two affinities at once (which might be explained as the loss or suppression of two opposite polarities); but that an element may be now an artiad and now a perissad, *i.e.*, even or odd in the number of its bonds.

The subject is not well understood, but it presents a good opportunity for acting on the lesson taught by Prout's "law," not to be captivated by a beautiful idea, but to stick closely to facts.

It would be impossible at this time to follow all the subsequent contributions to the theory of chemistry, but the most superficial sketch of the subject would be incomplete without studying an extraordinary discovery of which the advent had been preparing long before its announcement by Lothar Meyer and D. Mendelejeff. The latter pointed out that if the atomic weights of the light elements (or those with atomic weights from one to thirty-six) be arranged in two lines of seven each, a natural grouping is effected, thus :—

Li—7. Be—9.4. B—11. C—12. N—14. O—16. F—19. Na—23. Mg—24. Al—27.3. Si—28. P—31. S—32. Cl—35.5.

In these two lines two periods are passed over. From left to right in each, with the increase of atomic weight is a change from the most electro-positive to the most electro-negative, while the elements in the centre are nearly neutral. Again, from the beginning of the second period, elements of the same kind come to stand under one another. The same might be shown to be true in their behaviour in forming compounds with oxygen. Again the metals are on the left and the non-metals on the right. The specific gravities increase, and the atom volumes (or the atomic weights divided by the specific gravities), and all other physical and chemical properties which have been examined, change by regular gradations in vertical or horizontal lines. Without pursuing this subject into its curious details it is apparent that there has been some law exemplified in the production of these elements; a condition of things which is cyclical in its action or, as it is called, periodic. From the data obtained it was possible to construct a table which, while containing all the known elements, contained gaps in certain places where (according to the analogy of the periods), elements

* Von Meyer's admirable and impartial work on the History of Chemistry (Leipzig, 1889), a most valuable contribution to the science and a fitting supplement to Kopp's, has been largely drawn upon.

ought to have been, but none had been discovered. From the position of these gaps it was even possible to prophesy from the analogy of elements in similar positions of other periods, that, if discovered, the new elements filling these gaps would have properties intermediate between those occupying places before and after it, in regard to fusing point, solubility, specific heat, positive or negative polarity, &c.

After the announcement of this periodic law, chemists were impatient for a verification of its accuracy, and in the discovery of the newest metals, gallium and germanium, those predictions were found to have been well founded.

As no better test of a theory can be had than its use as a basis of prediction, the periodic law may be said to have been proved, and to be evidence of a profound and intimate connection between the elements.

What the connection is has not been certainly ascertained, but a bold and beautiful hypothesis was enunciated in 1886, by one of the greatest of the master minds of our age, in his Presidential Address before the Chemical Section of the British Association for the Advancement of Science, William Crookes.*

A skeleton of the views in this paper is as follows :—

Norman Lockyer said that a terrestrial element is an exceedingly complex thing, broken up into simpler things at the temperature of the sun.

Sir Benjamin Brodie in 1867 said, " We may conceive that in a remote time or in remote space there existed formerly, or may exist now, certain simpler forms of matter than we find on the surface of our globe."

Professor Stokes, in referring to a line in the spectrum of the nebulæ, remarks :—It may possibly indicate some form of matter more elementary than any we know on earth."

Crookes holds that the unequal distribution of elements in the earth's crust is evidence in favour of their composite nature.

The probability of such rare metals as yttrium, ytterbium, &c., having been brought together by chance in a few uncommon minerals and in a few localities, is very small. They would rather seem to have been formed severally from some common material placed in conditions in each case nearly identical ; and the existence of other groups of metals, as nickel, cobalt, and the two platinum groups furnishes additional ground for this supposition. Another argument in favour of their composite nature is that of the organic compound radicles.

Dr. Carnelley at the previous meeting (1885) had shown that on the supposition of two chemical elements, one with an atomic weight of twelve and the other of two— all the features of periodicity in Mendelejeff's series could be produced by their combination, and every well known element reproduced except hydrogen.

Dr. E. J. Mills considered the elements we now have as the result of successive polymerisations.

All these observations Crookes has thrown into a diagram by which is represented the hypothetical condensation of the original " fire mist," out of which the universe was derived, and which contained not matter but the potentiality of matter. In this condensation due to the gradual lowering of the temperature, another force than that of heat was at work—a force which he supposed not very different from electricity. As the temperature was lowered the elements congealed one by one out of the protyle in the form of atoms, of which the weight depended upon the temperature at the time of this formation, and the properties due to the electrical phase at the time of their birth. But the potential energy of the atom was greatest in the first that were thus condensed and more sluggish in the last when the temperature was lowest and the electrical force least.

We must be warned by the very beauty of this con-

* See Address of William Crookes, President of the Chemical Section Brit. Assoc. for the Adv. of Science, at the Birmingham Meeting, 1886. (Report B. A. A. S., 1886, p. 558.)

ception that it is but the effort of a superior mind to materialise for us the successive phenomena which it sees in imagination, and not a register of observed phenomena or a proven genesis. Yet it is impossible to conceive of the regularity and accuracy with which the labour of a century is fitted into that scheme without feeling that it contains more than a figment of the fancy.

At least nothing greater and nobler has been attempted in our science since its inception, and whether it be finally assigned its place among the great theories of the world or not, it will, undeniably, through its broadening of our views and its enlarging of our conception, have been a help to the progress of chemical theory.

NOTICES OF BOOKS.

The Foundations of Chemistry. (Grundlagen der Chemie). By D. MENDELEJEFF, Professor in the University of St. Petersburg, Translated from the Russian by L. JAMIN and A. THILLOT. St. Petersburg : Ricker, 14, Nevsky Prospect. (Large 8vo.)

THIS work is certainly not one of those voluminous compliations which aim at telling us everything that has been ascertained in chemical science. Still less is it a cram-book from which the intending examinee may gain a superficial varnish of knowledge, which it is hoped will satisfy the requirements of some Board or Department. Its *raison d'être* lies in presenting a condensed but clear view of the philosophy of chemistry.

The Introduction opens with the words—" Chemistry concerns itself with the investigation of the homogeneous substances of which all bodies of the world are composed." Two words here, "investigation " and "substances," words which the many hear, read, or use without attention, are made the subject of two suggestive notes. Says the author, " If anything is to be explored, something else must be assumed as given without investigation or as already known." As examples he gives the axioms of geometry and the faculty of organisms to reproduce themselves,—a concept which is for the present inexplicable.

We cannot refrain from envying those nations which can use, in place of our " phenomenon " and its paronymes, a word "understood of the people," and incapable of being juggled with. It is not soothing to our feelings to hear quacks boasting of their success as " phenomenal."

In classifying the Sciences, Prof. Mendelejeff—like some other Continental authorities — uses the word " biology " in a different acceptation from that which prevails amongst us. He speaks of " physiology " *and* biology, while with us biology is a whole of which physiology is one part.

The author distinctly recognises Lavoisier as the founder of modern chemistry, and as fully recognises that " matter is neither created nor destroyed." He insists that the highest scientific reputation must be ascribed not to the man who first announces a truth, but to him who can secure its recognition. But such men can arise only in consequence of the work of many others, and by means of long accumulation of materials.

It will be remarked that Prof. Mendelejeff is distinctly opposed to the rising doctrine of transmutability of the elements. If such conversions were possible we might, he holds, expect to find the simple bodies undergoing mutual transmutations. Such expectations, however, are contrary to the very essence of transformation, whether among elements or organisms. We consider existing animal species as having been developed not from each other, but from earlier less-differentiated forms. In like manner we do not seek to derive iodine from bromine or chlorine, but to trace all the members of this group from

some primæval generalised halogen. That we are not yet able to prove how the elements have been formed from one original matter, protyle, may be conceded.

The author asserts that "it has been established by spectral analysis that the simple bodies exist on the most remote stars." True; but the astrophysicists teach us that the number of kinds of simple bodies is smallest in the white stars, which we have reason to suppose are the hottest, but is larger in those of presumably lower temperatures. Hence it seems fair to infer not that certain "elements" are decomposed by the highest temperatures, but that they are only formed as a star gradually cools down.

Concerning some of the recognised or supposed simple bodies the author entertains doubts,—e.g., erbium, terbium, samarium, neodymium, &c. He thinks that they may consist of mixtures of other known bodies.

Regarding chemical affinity and its laws Prof. Mendelejeff writes:—"As regards the chemical mechanism and the molecular world, Lavoisier and Dalton may be compared with Copernicus and Kepler; its Newton has not yet appeared."

Concerning solutions the author is of opinion that the unity of our chemical concepts cannot be reached so long as a physico-mechanic view predominates concerning indefinite compounds (e.g., solutions). "In seeking to bring solutions under the concepts of the Daltonian atomic theory, I hope to arrive not only at a comprehensive and harmonious chemical theory, but to give an impulse to new researches and observations which may either confirm this view or substitute for it a more complete and a simpler theory."

This book is entitled to many and attentive readers, and few will rise from its conscientious perusal without profit. They will find in the author a judicious and thorough guide through the widening fields of chemical philosophy.

CORRESPONDENCE.

ESTIMATION OF FATTY MATTER IN TURKEY-RED OIL.

To the Editor of the Chemical News.

SIR,—Mr. Williams finds my process to be inaccurate (see CHEMICAL NEWS, vol. lxiv., p. 15) when compared with his wax method, and against three samples of prepared oil containing theoretical percentages of fatty matter; but he gives no details as to how the theoretical fatty matter in these samples were found or calculated. Mr. Williams has also made the mistake of using 5 c.c. of 1 to 2 HCl instead of 0·5 c.c. of 1·2 sp. gr. HCl,—a point of some importance,—and charges me with the grave error of not comparing the ether extraction method with some standard process. Where is the standard process to be found? is it the wax process? My modified process, like Mr. Williams's, requires very careful working, and, when carefully carried out, I believe there is little or no decomposition of the fatty matter.—I am, &c.,

J. A. WILSON.

Tottington, July 15, 1891.

ESTIMATION OF ALUMINIUM IN CAST-IRON.

To the Editor of the Chemical News.

SIR,—I notice in CHEMICAL NEWS (vol. lxiii., p. 172) a method, by M. A. Carnot, for the estimation of aluminium in cast-iron and steel, which is substantially the same as that originally described by Mr. Stead. M. Carnot does not in any way allude to Mr. Stead's method, and I think

it is only fair that the attention of your readers should be called to this fact.—I am, &c.,

A. S. BLECKLY.

The Laboratory, Bewsey Forge,
Warrington, July 2, 1891.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxiii., No. 1, July 6, 1891.

Study of Carbon Tetraiodide.—Henri Moissan.—Boron teriodide furnishes several new reactions. On projecting boron iodide into dry, cold chloroform, the iodide is dissolved and the mass quickly congeals. After a few days the gelatinous matter disappears and the bottom of the vessel is filled with a fine crystallisation of iodoform, whilst vapours of boron chloride escape continuously. Phosphorus reacts energetically upon boron iodide. If we prepare a solution of boron iodide in pure dry carbon disulphide, and add ordinary phosphorus free from water, there is produced a dense reddish powder, from which, on heating, there is evolved a small quantity of phosphorus and phosphonium iodide. The residue is a white powder containing phosphorus and boron. This boron phosphide, infusible at a red heat, is not acted on by nitric monohydrate. It is decomposed by watery vapour into hydrogen phosphide and boric acid, and resembles in its properties the boron nitride of Deville and Woehler. If boron teriodide is permitted to react upon carbon tetrachloride there is readily obtained boron trichloride and carbon tetraiodide. This compound, when very dry, if heated *in vacuo* to between 90 and 100°, sublimes very slowly in fine red crystals, having the lustre and the transparence of the synthetic rubies of Fremy and Verneuil. Their composition is represented by the formula C_2I_4.

Combinations of Camphor with the Aldehyds: New Method of Forming the Alkoylcamphors.—A. Haller.—This paper does not admit of useful abridgment.

Calculation of Molecular Volumes.—G. Hinrichs.—The author describes a statical and a dynamical method which agree in their results.

An Explosive Compound formed in the Action of Baryta-Water upon Chromic Acid in Presence of Oxygenated Water.—E. Péchard.—There is produced a precipitate of a chamois colour, which when dry detonates violently if struck or heated. Its composition is possibly BaO_2CrO_3.

Determination of Small Quantities of Boric Acid.—F. Parmentier.—The waters upon which the author has experimented were evaporated, when they give rise to precipitates insoluble in water, and containing all the boric acid, along with the chief part of the silica, the phosphoric acid, and the arsenic. On treatment with hydrochloric acid they yield liquids which, if evaporated at low temperatures, do not lose any boric acid. The matter on being taken up in water acidulated with hydrochloric acid, and then treated with ammonium nitrate slightly ammoniacal, leave a residue containing the iron, alumina, manganese, arsenic, and phosphoric acid, whilst the boric acid remains in solution. The liquid is rendered distinctly acid either with dilute sulphuric or hydrochloric acid, and is then divided into two exactly equal portions. In one of these portions the acidity is determined, using helianthine as an indicator, whilst in the other a similar acidimetric determination is effected with the tincture of litmus as prepared by De Luynes. The nor-

mal alkaline liquid used is caustic soda. The quantity of boric acid is deduced from the difference of the results obtained in the two operations. The change of colour with litmus takes place when sodium biborate has been formed.

Journal fur Praktische Chemie.
New Series, Vol. xliii., Parts 7 and 8.

Further Observations on the " Black Sulphur " of Magnus.—Fr. Knapp.—The preparation of Magnus contains sulphur certainly in two different conditions; the one part as an integral constituent of the process of carbonisation, the other in the free condition. The free sulphur cannot possibly be the ordinary yellow kind, differing totally in its behaviour. The temperature at which it is converted into vapour is much higher than the boiling-point of yellow sulphur; its vapour is not brown but colourless, and when heated with access of air it yields sulphurous acid before the appearance of a visible red heat, and without any phenomena of combustion.

Researches from the Laboratory of the University of Freiburg.—These researches comprise papers by Ad. Claus on the constitution of benzol, by Ad. Claus and E. Krauseon thymol, and by Ad. Claus on the formation of alkyl-ketones from the halogen derivatives of aromatic carbon-compounds.

On the Betaines of the Pyridine Bases.—Martin Krüger.—By means of the methods of Hofmann and Liebreich the betaines of pyridine, β-picoline, and ethyl piperidine can be very conveniently obtained. The betaines of the pyridine series approximate in their entire behaviour to the betaines of the fatty series.

The Derivatives of Salol.—W. Knebel.—The compounds examined are acetylsalol and the nitro-derivatives of salol.

The Addition of Sodium Acetacetous and Sodium Malonic Ethers to the Ethers of the Non-Saturated Acids.—Michael and Paul C. Freer.—The continuation of an extensive memoir.

The Faculty of Reaction of Monochlortrimethylene and Certain Allied Compounds.—E. Gustavson.—These experiments show that among all the isomers of the formula C_3H_5Cl hitherto examined in this direction, monochlortrimethylene is the most stable if exposed to the action of alcoholic potassa.

A New Quantitative Separation of Manganese and Zinc.—P. Jannasch and J. F. McGregory.—Already inserted.

On Dimolecular Cyanethyl.—P. S. Burns.—The author has submitted dicyanethyl to the action of acid chlorides and of hydroxylamine. The investigation is not yet complete.

Revue Universelle des Mines et de la Metallurgie.
Series 3, Vol. xiv., No. 2.

Gasometric Determination of Oxygen in Gaseous Mixtures. — Prof. L. L. de Koninck. — (Inserted at p. 45).

Volatility of Iron.—Dr. Fleitmann.—Experiments on soldering together iron and nickel have led the author to important results on the volatility of the former metal and its atomic penetration. The adherence of the two metals was such that it was impossible to separate them by mechanical action, and chemical analysis demonstrated a true alloy—an intimate combination, although the soldering had been effected at a temperature 500 or 600° below their point of fusion. Other experiments proved the volatility of iron at a cherry red heat. Two superimposed plates of iron and nickel having been submitted to a similar heating, the iron passed over to the nickel in notable quantity without either soldering or adhesion of

the surface. Over the entire sheet of nickel there was formed an alloy of iron, which in sheets of 1 m.m. penetrated to 0·05 of their thickness, and contained a mean of 24 per cent of iron. This passage of iron to nickel is not reciprocal. This volatility of iron is still unexplained, and we do not know whether it is due to traces of ferric cyanide, chloride, or carbide.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. vi., No. 62.

Communications and Reports presented by M. Davanne on the Present Applications and Procedures of Photography. — The author recognises in photography three stages; the first, that of the Daguerre plate, the second, that of collodion and its derivatives, and the third, or present phase, characterised by the exclusive use of silver gelatino-bromide. He ascribes the early failures in the use of bromine preparations to the employment of silver bromide alone, to the action of yellow light, and to the absence of an excess of soluble bromides. In a report made by M. Davanne on behalf of the Committee of Constructions and the Fine Arts it is proposed to dispense with the lens, using in its stead merely a fine hole. Further reports by the same author treat of photography in balloons, of aërial photography by means of kites, and on the " Obturator " of MM. Londe and Dessoudeix.

Basic Slags : their Use in Agriculture.—M. Campredon.—The writer upholds the employment of basic slag as a phosphatic manure, but points out that to be a " complete manure " it requires the addition of potassa and of nitrogenous matter. He does not consider the iron and manganese oxides as injurious.

Vaseline, Petroline.—M. Riche.—An account of the uses of the mineral fats in pharmacy. Its abuses in confectionery, &c., and the means for its detection in articles of food are not referred to.

MISCELLANEOUS.

The Atomic Weight of Lanthanum.—Bohuslav Brunner (*Ber. der Deutsch. Chem. Gesell*).—The author determined this atomic weight of lanthanum by converting lanthanum oxide into sulphate, and obtained the following result : $La(O=16)=138·21$. This value is identical with those obtained by Cleve (*Bull. Soc. Chim.*) and Bettendorff (*Ann. Chem. and Pharm.*). The material was obtained from impure lanthanum oxide by fractionated exhaustion with ammonia nitrate, and contained therefore the most positive earth of cerite. It was totally free from " didymium," and displayed in the spark spectrum of the chloride no lines belonging to other earths. The author adds in a note, " I designate as didymium the mixture which in addition to neodymium and praseodymium certainly contains other earths."

ERRATA.—P. 33, col. 1. At the International Congress of Hygiene and Demography, the paper to be read by Dr. Russell is entitled " Town Fogs and their Effects," and that by Sir A. Mitchell and Dr. Buchan " The Influenza and Weather of London."

THE CHEMICAL NEWS.

VOL. LXIV., No. 1653.

ON THE NATURE OF SOLUTION.
(No. III.).

By J. ALFRED WANKLYN and WILLIAM JOHNSTONE.

CONTINUING the investigation, we are now prepared to announce that we have found a new chemical, or physico-chemical, function of wide generality, viz., $i - i_I =$ the condensate. It is the quantity of water condensed by one grm. of a substance when that one grm. enters into the 100 c.c. or the litre of solution, and *not* overflowing out of the 100 c.c. or the litre, as it would do in the case of sugar.

Our investigation is now sufficiently advanced to enable us to say that the condensate bears an atomic relation to the substance dissolved. The condensate is also quite distinct from water of crystallisation. In the instance of the sulphates, the condensate is large, but it is not the same as the water of crystallisation. We expect that the salts of each particular alkali will be characterised by the condensate belonging to the different salts. The following is a tabular statement of soda and potash salts :—

Soda Salts.

	Found.	Theory.
$2NaCl + H_2O$	0·140	0·153
$3NaBr + H_2O$	0·054	0·058
$3NaI + H_2O$	0·042	0·040
$4NaHO + 5H_2O$	0·568	0·562
$3NaNO_3 + 2H_2O$	0·146	1·141
$Na_2OSO_3 + 2H_2O$	0·281	0·253
$3NaHOCO_2 + 2H_2O$	0·132	0·143

Potash Salts.

	Found.	Theory.
$3KCl + 2H_2O$	—	—
$3KI + H_2O$	0·035	0·036
$3KNO_3 + H_2O$	0·058	0·059
$3KClO_3 + H_2O$	0·063	0·049
$2K_2OSO_3 + 3H_2O$	0·152	0·155
$2KHOCO_2 + H_2O$	0·097	0·090
$KHO + H_2O$	0·341	0·321

and here follows some of the experiment details.

Iodide of Potassium.

The specific gravity of a solution containing 10·00 grms. per 100 c.c. of solution was 1·07020.

$$i \quad = 0·702$$
$$i_I \quad = 0·667$$
$$\overline{i - i_I = 0·035}$$

$3KI + H_2O$ requires $i - i_I = 0·036$.

Chlorate of Potash.

Specific gravity of the solid was found 2·132 at 21° C. A solution containing 5·00 grms. per 100 c.c. had specific gravity 1·02970.

$$i \quad = 0·594$$
$$i_I \quad = 0·531$$
$$\overline{i - i_I = 0·063}$$

$3KClO_5 + H_2O$ requires $i - i_I = 0·049$.

Bicarbonate of Potash.

Specific gravity of the crystals found 2·104. A solution containing 10 grms. per 100 c.c. had specific gravity 1·06220.

$$i \quad = 0·622$$
$$i_I \quad = 0·525$$
$$\overline{i - i_I = 0·097}$$

$2KHOCO_2 + H_2O$ requires $i - i_I = 0·090$.

Caustic Potash.

The specific gravity of solid caustic potash was found to be 2·00 at 20° C. The specific gravity of a solution of caustic potash containing 10 grms. KHO in the 100 c.c. of solution was 1·08415. Therefore—

$$i \quad = 0·841$$
$$i_I \quad = 0·500$$
$$\overline{i - i_I = 0·341}$$

$KHO + H_2O$ requires $i - i_I = 0·321$.

Caustic Soda.

The specific gravity of the solid was found to be 1·923 at 20° C. A solution containing 3·68 grms. per 100 c.c. had a specific gravity 1·03930. Therefore—

$$i \quad = 1·068$$
$$i_I \quad = 0·480$$
$$\overline{i - i_I = 0·588}$$

$4NaHO + 5H_2O$ requires $i - i_I = 0·562$.

Caustic Lithia.

Specific gravity of the solid 1·495 at 20° C. A solution was made and its specific gravity taken.

$$i \quad = 0·924$$
$$i_I \quad = 0·331$$
$$\overline{i - i_I = 0·593}$$

$LiHO + H_2O$ requires $i - i_I = 0·750$. $5LiHO + 4H_2O$ requires $i - i_I = 0·600$.

We are prepared with a further theoretical development illustrated by the case of sulphate of copper, and can now show a *completed* volumetric relationship.

The Laboratory, 13, Fish Street Hill, E.C.
July 20, 1891.

COLORIMETRIC METHOD FOR ESTIMATING GALLOTANNIC ACID, GALLIC ACID, AND TANNIC ACID IN BARKS, &c.

By SAMUEL J. HINSDALE, Fayetteville, N.C.

DISSOLVE 0·04 grm. potassic ferricyanide in 500 c.c. water, and add to it 1·5 c.c. (about 22 drops) liquor ferri chloridi. Call this *iron mixture.* (The best way to prepare this is to dissolve 0·4 grm. potassic ferricyanide in 500 c.c. water, and make 50 c.c. of it up to 500 c.c. and add the liquor ferri chloridi.)

Dissolve 0·04 grm. " pure tannin " (gallotannic acid) which has been dried at 212° F. in 500 c.c. of water. Call this *tannin solution.* (The best way to prepare this solution is to dissolve 0·4 grm. of the dry gallotannic acid in 500 c.c. water, and make 50 c.c. of it up to 500 c.c. with water.)

Exhaust 0·8 grm. oak-bark with boiling water, and make it up to 500 c.c. with cold water. (It is well to exhaust 8 grms. of the bark, and make the infusion up to 500 c.c., and take 50 c.c.—equal to 0·8 grm. bark—and make it up to 500 c.c. for the assay.)

Place six 2-ounce clear glass tumblers (or beaker glasses) on a white surface, and in one of them, *with a dropping pipette* (about four inches long and one-quarter inch wide) *about half filled*, put *five drops* of the infusion of bark, and in the others, *with the same pipette* (after

rinsing), put 4, 5, 6, 7, and 8 drops of the " tannin solution." (The drops of the infusion and of the " tannin solution " must be uniform. The use of the same pipette, about half filled, *insures that*.) (The pipette should be made so as to deliver *about* 50 or 60 drops per minute, 20 drops of which should weigh *about* 1 grm.)

Now add to each about 5 c.c. of "iron mixture" (it is convenient to have a measure for this—a homœopathic vial will answer), and in about one minute add to each tumbler about 20 c.c. water, and *within three minutes* observe the shades of colour. The number of drops of " tannin solution " used in the tumbler which corresponds in shade of colour to the tumbler containing the infusion of bark *indicates the percentage* of gallotannic acid in the bark, — *i. e.*, if it is the one in which seven drops were placed the gallotannic acid strength of the bark is *seven per cent.*

It is best to observe the shades of colour horizontally rather than vertically, and to hold up the infusion tumbler, with the one which most nearly corresponds, opposite to a white wall, with your back to the light.

The above is written for *oak bark*, but the same process will answer for any substance containing less than 10 per cent of gallotannic acid.

For substances containing between about 10 and 20 per cent it is best to dilute the infusion with an equal part of water and proceed as above, using *five drops* of the *dilute* infusion, and for the answer double the result. Thus, if the diluted infusion of tea required eight drops of " tannin solution " to correspond, call the percentage *sixteen.*

For substances containing less than 1 or 1½ per cent, exhaust *eight grms.* instead of 0·8 grm., and take *one-tenth* of the result for the answer. For substances containing more than 20 per cent—as galls, sumach, catechu, &c.— you may dilute the infusion with two, three, or more times its bulk with water, and calculate as above (as with tea), or you may use one, two, three, or four drops of the undiluted infusion in the first glass, and make the calculation thus :—*i. e.*, As the number of drops of infusion used is to the number of drops of " tannin solution " used (to correspond), so is 5 to the answer; thus, suppose *two* drops of infusion were used, and the corresponding tumbler contained *fifteen* drops of " tannin solution "—2 : 15 :: 5, answer 37·5 per cent.

The object in diluting the infusions is because the infusion glass may be of too deep a blue shade. It is better that it should just produce a *light* blue.

The tumblers must be perfectly clear and clean.

The " iron mixture," " tannin solution," and infusion must be freshly prepared, and not exposed to the rays of the sun. The water used must be free of iron and tannin.

The above was published in the *American Journal of Pharmacy*, March, 1890, and is for the estimation of *gallotannic acid* only.

The same method can be used for the estimation of gallic acid; and by deducting the percentage of gallic acid found from the percentage of gallotannic acid found, the percentage of tannin in the bark can be determined with much accuracy.

To estimate the gallic acid (having previously estimated gallotannic acid), precipitate the tannin from 50 c.c. of the infusion—equal to 0·8 grm. bark—by mixing with it 0·2 grm. alum and 20 c.c. solution of gelatin (3 grms. to litre). After mixing well, make it up to 250 c.c. with water, and filter off a little of it. Put five drops of the filtrate in the first glass, and proceed according to the method, using a solution of 0·02 grm. pure dry gallic acid to a litre of water, in place of the " tannin solution." (To prepare this solution, dissolve 0·2 grm. of the gallic acid in 500 c.c. of water, and make 50 c.c. of it up to a litre, with water.)

One-eighth of the number of the drops of the gallic acid solution used to produce the same shade of colour

as is produced in the glass containing the filtrate will indicate the percentage of gallic acid in the bark, which, deducted from the percentage of gallotannic acid found, will tell the percentage of tannin in the bark.

Barks vary very much in gallic acid strength; for instance, white oak contains from 2 to 2 5 per cent, while hemlock contains only about 1 per cent.

It is all important that the solutions and the infusion be freshly prepared. The " iron mixture " is decomposed a little in twenty-four hours. It must not be exposed to the rays of the sun. The " tannin solution " changes in a few days. This solution must be made with pure gallotannic acid which has been dried at 212° F.

The infusion of bark undergoes some change in a few days.

The glasses used must be clean and clear, and placed on a white surface.

CONTRIBUTIONS TO MICRO-CHEMICAL ANALYSIS.*

By H. BEHRENS.

(Continued from p. 41).

——

X.—*Manganese.*

1. With oxalic acid. Star-shaped aggregates of prismatic twin crystals, measuring 100—120 micro. Oblique terminal plane of 60°. Straight extinction. Single crystals in presence of zinc, cobalt, and nickel. Alkaline salts interfere, and strong acids more so. Limit of the reaction about 0·001 m.grm. With potassium oxalate about 0·0005 m.grm.

2. With phosphoric salt and ammonia. Hemimorphous crystals of the rhombic system of 40 micro., similar to those of ammonium magnesium phosphate. Limit at 0·0005 m.grm. Mn.

On account of the rapid oxidation of ammoniacal solutions of manganese, the port-object must be heated with the acid manganese solution, and the mixture of phosphate and ammonia added subsequently. For closer examination the crystals adhering to the glass may be rinsed off, and potassa or soda-lye be added along with a drop of hydrogen peroxide. The crystals then turn brown, but retain their form.

3. With nitric acid and potassium chlorate. Blackish brown flocks; on careful evaporation a strongly adhesive black-brown film of manganese peroxide, which may be rinsed off and tested as in 2, or before the blowpipe with soda. Limit of the reaction at 0·0002 m.grm. M. All the reactions described fall short of the above-named blowpipe reaction, which is at the same time exceedingly characteristic.

XI.—*Cobalt.*

1. With potassium nitrite and acetic acid yellow granules 2—4 micro.; from hot dilute solutions yellow cubes and octahedra 12—20 micro., and belonging to the compound $K_5CoN_{12}O_{24} + 3H_2O$. Valuable, as nothing but cobalt is precipitated, and the deposit adheres to the glass. Limit of the reaction at 0·0001 m.grm. Co.

In an ammoniacal solution no precipitate is produced by nitrite, but merely an intense yellowish brown colour. Acetic acid then occasions a precipitation. There is danger of confounding cobalt with nickel if calcium, strontium, or barium is present. (See Nickel 1).

2. With ammonium-mercury sulphocyanide. Splendid blue rhombs, mostly grown together in lumps and globes of peculiar form. With zinc and cadmium light blue mixed crystals. Limit of the reaction at 0·0003 m.grm. Co.

A solution of mercury sulphocyanide in a small excess of ammonium sulphocyanide is a good reagent in order to detect cobalt in presence of many other metals. With

* *Zeit. Anal. Chemie.*

nickel it gives no precipitate; with copper greenish rhombs and spears which appear *after* the blue crystals of cobalt. Hot water and also strong acids dissolve the crystals. Ammonia destroys the colour, which is restored by acetic acid.

3. With phosphor salt and ammonia. Crystals of the type of ammonium-magnesium phosphate, extended in length, and in presence of much sal-ammoniac and ammonia increasing to 100 micro. Limit of the reaction at 0·00002 m.grm. Co.

The precipitation is to be effected in the manner described under Manganese 2. The crystals are coloured brown by caustic soda and hydrogen peroxide. The blue crystals of reaction 1 are produced in their place by acetic acid and ammonium-mercury sulphocyanide. Nickel may be excluded as a preliminary by precipitating cobalt and manganese from an ammoniacal solution by means of hydrogen peroxide.

XII.—*Nickel.*

1. With potassium nitrite and lead acetate a yellow powder; from dilute solutions small yellow crystals of the triple salt, $KNiPbN_6O_{12}$, exactly similar to those of potassium cobalt nitrite. A quite similar but tardy reaction with barium, strontium, and calcium. Limit of the reaction at 0·000008 m.grm. Ni.

Potassium nitrite occasions no visible change in ammoniacal solutions of nickel. A granule of lead acetate occasions a deposition of pulverulent salts of lead. If acetic acid is then added, after gentle heating the yellow precipitate appears heaped up upon and around the salt of lead. It appears still instantaneously in the 6000 fold dilution of the nickel sulphate.

2. With phosphor salt and ammonia. Hemimorphous crystals, shorter than those of cobalt. They are not turned brown by caustic soda and hydrogen peroxide. Limit of the reaction at 0·00001 m.grm. Ni.

Precipitation with oxalic acid, proposed by Haushofer for distinguishing cobalt from nickel, cannot be recommended. For cobalt the limit of precipitation is at 0·0002 m.grm., but for nickel at 0·001. Cobalt oxalate falls rather sluggishly in the shape of fine needles and stars; nickel oxalate follows afterwards as a fine powder which renders the drop turbid. The ammoniacal solution of the oxalates displays a reversed behaviour on the evaporation of the ammonia. The nickel oxide falls after some time seemingly unchanged, whilst cobalt may remain in solution for hours in presence of much ammoniacal salt.

XIII.—*Zinc.*

1. With sodium bicarbonate. Colourless tetrahedra, 6—20 micro., of the compound $Na_6Zn_8C_{11}O_{33}+8H_2O$, and crossed twin crystals of the same compound. Refracts light strongly, and adheres to the glass. Limit of the reaction 0·00001 m.grm. Zn. Limit of the immediate reaction at the 40,000 fold dilution of zinc sulphate.

From acid solutions sodium bicarbonate precipitates cadmium immediately in granules and zinc after about a minute in fine flocks. With an excess of alkaline carbonate there are gradually formed tetrahedra, whilst the liquid becomes clearer. With potassium and lithium the crystals are larger with predominating twin formation. Salts of ammonium, calcium, magnesium, and cadmium interfere. In ammoniacal solution there is immediate precipitation of cadmium, and no turbidity or formation of tetrahedra beginning at the margin. Magnesium interferes seriously, and must be previously removed by the cautious addition of phosphate.

2. With oxalic acid we obtain, even in presence of a considerable quantity of free hydrochloric acid, short prisms, generally rounded, of zinc oxalate,

$$ZnC_2O_4+2H_2O,$$
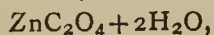
of 20—25 micro. Easily soluble in ammonia. On its evaporation there are formed manifold ramified and curled rosettes of 200—700 micro. Cadmium interferes with their formation, and magnesium more so. In acid solu-

tions magnesium may cause the formation of a double oxalate in pale hexagonal tables of 40—60 micro. Sal-ammoniac opposes its formation. Limit of precipitation by oxalic acid 0·0001 m.grm. Zn.

3. With ammonium mercury sulphocyanide. From dilute solutions, and with a considerable excess of ammonium sulphocyanide, rectangular rods, otherwise forked and dendritic, often curiously curved and feathered. Magnesium has no influence. Cadmium slightly simplifies the formations. The colouration by cobalt (see Cobalt 2), may be used to detect zinc and cadmium in these precipitations. Limit of the reaction at 0·0001 m.grm. Zn.

4. With potassium ferricyanide. A yellow powder, but from very dilute liquids yellow cubes of 5—12 micro. Cadmium gives the same reaction. Limit at 0·00005 m.grm. Zn.

Zinc phosphate is easily soluble in ammonia, but does not form with it a crystalline double salt. On treating the arseniate in a similar manner we obtain crystals very similar to those of ammonium magnesium phosphate.

Zinc chromate resembles strontium chromate both in its appearance and in the conditions of its precipitation.

(To be continued).

AËRATED MILK: DETERMINATION OF AIR.

By H. JOSHUA PHILLIPS, F.I.C. F.C.S.

MILK which has been deprived of its fat, and aërated with carbonic anhydride by Crampton's patent process, is now recommended by the medical profession for invalids whose digestive organs are incapable of assimilating raw milk.
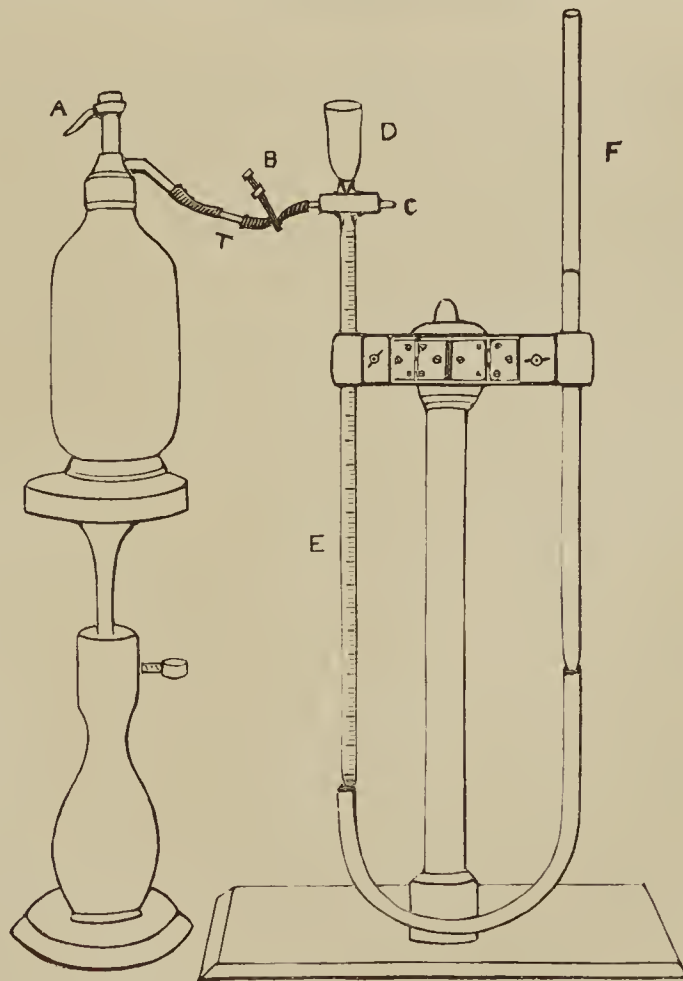
The carbonic anhydride is forced into the separated milk contained in glass syphon bottles at a pressure of 80 lbs. per square inch, and from which quantities can be drawn as desired, the residual milk retaining its original flavour.

In order that the milk should keep for some time it becomes essential that the precipitation of the casein, &c., should be prevented by checking the propagation of lactic fermentation. In the course of some biological experiments the writer is instituting to this end, the determination of the amount of air present in the aërated milk became necessary, and the following is a sketch of the apparatus and details of the method employed. The tube T having first been filled with water to expel air. one end is fitted on to the end of the exit tube of the syphon bottle containing the milk, and the other to the three-way tube tap of Lunge's improved nitrometer previously filled with mercury. The tube T is supplied with a clip, B. The clip B having been relieved, the valve A is opened, when liquid and gas are forced into E. After about 40 c.c. of gas have been obtained, the valve A is dropped and the clip B closed. F is now lowered until the pressures are equalised. The temperature and pressure having been taken, the volume is read off. About 5 c.c. of a concentrated solution of caustic potash are now run into the funnel, D, and F lowered until the mercury is below the level of that in E ; and by manipulating the stopcock, C, the liquid is made to run into E, the CO_2 is rapidly absorbed, and the air remains. After correcting for temperature and pressure its volume is obtained.

Stratford, London, E.

ON THE
MOLECULAR WEIGHTS OF LIQUIDS AS EVINCED BY THEIR BOILING-POINTS.

By H. M. VERNON.

OF the methods for determining the molecular weights of bodies at present recognised, that depending on vapour density determinations can only give the molecular weight of a body when in the gaseous state, whilst those depending on Raoult's law of the molecular lowering of the freezing-point, on Van 't Hoff's law of osmotic pressure, and on the law of depression of the vapour pressure of a solution, only give the molecular weight of a body when dissolved in some solvent. Now, as the results obtained by Arrhenius, Ostwald, and others show that not only in some cases are the molecules existing in solution less complex in dilute than in concentrated solutions, but that these molecules frequently undergo a still further decomposition, and are split up into their free ions, which exist as such in the solution. It is therefore very probable that the molecules existing in a pure liquid undissolved in any other liquid, are in a more complex state of aggregation than when the liquid is so dissolved.

The object of this paper is to endeavour, by comparing volatile bodies as to some physical property, such as their boiling-points, to obtain some indication as to the probable value of their molecular weights when in the liquid state.

As a guide to the effect of molecular weight on the boiling-points of compounds, that afforded by certain well-known series of carbon compounds will at once be admitted. In these it is found that the addition of CH_2 to a compound generally raises the boiling-point about 19°, though the effect of introducing CH_2 into a compound already containing a considerable number of atoms of carbon is not so great as with a compound containing only a small number. Thus normal pentane and butane differ in boiling-point by 37°, undecane and decane by 22°, and nondecane and octdecane by 13°. Although the effect on the boiling-point of the introduction of CH_2 or other groupings into the molecule appears in many cases very simple, yet it must not be forgotten that in other cases this effect is greatly altered or even obliterated according to the structure the body formed takes up. An

idea as to the rise in boiling-point brought about by the doubling of the molecular weight of a body may be obtained from the behaviour of the members of the olefine series. Thus ethylene, C_2H_4, boils at − 105°, whilst butylene, C_4H_8, boils at − 5°. Octylene, C_8H_{16}, again, boils at 125°, and hexadecylene, $C_{16}H_{32}$, at 274°. Each doubling of the molecule is then attended with a rise in boiling-point of 100° or more.

It is proposed to first examine some of the principal inorganic liquids whose boiling-points are known, and to then study a few of the more important organic derivatives.

Of non-metallic inorganic compounds, one of the first that deserves notice is hydrofluoric acid. This body boils at 19·4°. Now hydriodic acid boils at about − 25°, hydrobromic acid at − 73°, and hydrochloric acid at about − 100°. We should therefore expect hydrofluoric acid to boil at about − 120°. The melting-points of these four bodies also vary in the same way. HI melts at − 55°, HBr at − 87°, HCl at − 115°, and HF at about − 40°. From vapour density determinations, Thorpe and Hambly have shown (*Chem. Soc. Journ.*, 1889, 163), that it is probable that the molecules of hydrofluoric acid at the boiling-point consist of H_4F_4. This is about the value which we should arrive at from the abnormal value of the boiling-point, which we see is about 140° too high. From comparison with the members of the olefine series, we should expect a greater difference than this, but it is impossible to compare at all accurately such widely different bodies as these, so all the conclusions that can be drawn are that the molecules of liquid hydrofluoric acid have a molecular weight greater than that expressed by the formula H_2F_2, and certainly not larger than H_4F_4.

The next important exception is to be found in water. Its congener, sulphuretted hydrogen, boils at − 61·8°, whilst even seleniuretted and telluretted hydrogen are gaseous at temperatures far below 0°. In order to arrive at a probable value of the boiling-point of water, supposing it to consist of simple H_2O molecules, we must compare some compounds of sulphur with the corresponding compounds of oxygen. There are, however, very few inorganic compounds fit for comparison, but such as are available show that sulphur compounds have considerably higher boiling-points. Thus $SOCl_2$ boils at 78°, but S_2Cl_2, in which the atom of oxygen is replaced by one of sulphur, at 138°, or 50° higher. Chlorine monoxide, Cl_2O, boils at 19°, whilst Cl_2S boils, with decomposition however, at 64°, or 45° higher. Again, ozone boils at − 106°, and SO_2, which may be considered as derived from it by substitution of one atom of sulphur for one of oxygen, at − 8°, or 99° higher. As will be shown later on, organic thio-compounds, with certain exceptions, boil at about 50° higher than the corresponding oxygen compounds. We may take it, therefore, that water, if consisting of simple H_2O molecules, would boil about 50° lower than H_2S, or at about − 110°. It therefore boils some 210° too high. We have seen that in the case of hydrofluoric acid, an increase in boiling-point of about 140° indicates a molecular weight greater than $(HF)_2$; water in the liquid state must therefore have at least the molecular weight expressed by the formula $(H_2O)_4$. The author has shown (*Phil. Mag.*, May, 1891), that water, on being cooled to 4°, probably undergoes molecular aggregation, so the molecules below 4° probably have a molecular weight at least that expressed by the formula $(H_2O)_8$. The fact that hydrogen peroxide, H_2O_2, a body of nearly double the formula weight, does not solidify even at − 30°, is additional support to the fact of liquid water having an abnormal molecular weight.

The next instances we come to are the oxides of chlorine. The monoxide, Cl_2O, boils at 19°, whilst the peroxide, ClO_2, boils at 9°. Now such a substitution of an atom of oxygen for one of chlorine is in other cases attended with a slight fall in boiling-point. Thus $SOCl_2$ boils at 78°, and SO_3 at 46°, or 32° lower. The oxides of chlorine in the liquid state probably therefore have

molecular weights expressed by their ordinarily received formulæ.

Elementary sulphur affords a marked exception. Its boiling-point is 448·4°, whilst oxygen, which in its compounds it so greatly resembles, boils at −182°. Selenium, which boils at 700°, and tellurium, which boils above this, must also have abnormal boiling-points. Thus bromine, whose atomic weight is more than double that of chlorine, boils at 63°, or only 97° higher than chlorine, whilst iodine boils at about 200°. Sulphur should therefore boil at about −90°, or at any rate very considerably below 0°. The fact that sulphur vapour just above its boiling-point consists of hexatomic molecules partly accounts for the high boiling-point, but even a treble molecular weight is not sufficient to explain a rise of over 500°. The molecules of liquid sulphur probably consist therefore of at least $(S_2)_6$ molecules, or molecules containing at least twelve atoms. This high value is confirmed by the fact of sulphur monochloride, S_2Cl_2, boiling at 138° only, or 310° lower than sulphur itself.

The fact that SO_2 boils at −8°, and that $SOCl_2$ boils at 78°, whilst SO_3, from which it may be considered as derived by substitution of two atoms of chlorine for two of oxygen, boils at 46°, shows that these bodies have normal molecular weights. Sulphuric acid, on the other hand is an exception, as it boils at 338°. Thus SO_2Cl_2 boils at 70°, and $SO_2\begin{cases}Cl\\OH\end{cases}$ at 158°, or 88° higher. Sulphuric acid, $SO_2(OH)_2$, should therefore boil at about 246°. Selenic acid also, which from its greater molecular weight would be expected to boil at a higher temperature, boils at about 280°, or 60° lower. Arguing from these data it is probably that the molecular weight is doubled, but it will be shown further on that it must be considered as having undergone a still further condensation, and that it consists in the liquid state of quadrupled molecules.

Selenium dioxide, SeO_2, is the next exception. It boils at about 300°, whilst from the fact that its congener SO_2 boils at −8°, we should expect it to boil below 100°. Again, selenium oxychloride, $SeOCl_2$, boils at 179·5°. Now the analogous body, $SOCl_2$, boils at 78°, or 86° higher than SO_2; $COCl_2$ also boils at 8°, or 86·2° higher than CO_2. SeO_2 we should therefore expect in a similar manner to boil some 86° lower than $SeOCl_2$, or at about 94°. The boiling-point of SeO_2 is thus some 200° too high. In the liquid state it must therefore consist of at least double molecules, and probably, from the conclusions arrived at in the analogous cases of HF and H_2O, of molecules of $(SeO_2)_4$.

The oxides of nitrogen showed no abnormalities in their boiling-points, except such as have long been accounted for by vapour density determinations. Thus the pentoxide boils at 45°, the tetroxide at 22°, the trioxide probably at a little below 0°, nitric oxide at below −100°, and nitrous oxide at −88°. The fact that the peroxide consists in the liquid state of N_2O_4 molecules is well shown by the boiling points, as if it consisted of NO_2 molecules it would boil at about −70°. Also it is evident that nitric oxide consists of NO molecules, for a liquid consisting of N_2O_2 molecules would boil at about −40°.

None of the halogen derivatives of phosphorus, arsenic, silicon, carbon, &c., appear to possess abnormal boiling-points, but they all show most striking regularity in increase of boiling-point on substitution of bromine for chlorine in the molecules. The same regularity of boiling-point exists for such fluorides and iodides as are known. A few of the chief chlorine and bromine compounds are here given, and also the increase in boiling-point for each atom of bromine substituted.

This serves to show how regular is the increase in boiling-point with substitution of atoms of bromine in a molecule for chlorine. The irregularities mentioned above can therefore be no fanciful ones, due merely to the different arrangements of the atoms the molecules are made up of, but must be due to some more powerful influence, the existence of which can only be accounted for by supposing them to be due to differences of molecular weight.

Of metallic compounds little can be said, as so few of their boiling-points or even melting points are at all accurately known. It is possible nevertheless to find some well marked exceptions. Thus antimony trichloride boils at 216°, and is therefore probably normal, for this value is higher than the boiling-point of arsenic trichloride, which boils at 134°, to about the same extent as this value is higher than that for phosphorus trichloride, which boils at 76°. Its melting-point is, however, 76°, whilst that of the pentachloride is −6°. In the solid state, therefore, the molecules of the trichloride must have double the value of the pentachloride molecules. Stannous chloride also forms an exception, for it boils at a low red heat, whilst stannic chloride, $SnCl_4$, boils at 113·9°.

Now, to take as nearly similar a case as is available, C_2Cl_6 boils at 185·5°, whilst C_2Cl_4 boils at 121°, or 64·5° lower. If the body C_2Cl_8 existed, it would boil somewhat above C_2Cl_6, $SnCl_2$ should therefore boil at about 80° lower than $SnCl_4$, or at about 40°. The molecules of liquid stannous chloride cannot therefore have a molecular weight smaller than that corresponding with the formula $(SnCl_2)_4$, and they probably have a considerably larger. The abnormal value for stannous chloride is rendered more evident when we consider that the bodies $TaCl_5$ and WCl_6, with very high molecular weights, only boil at 241·6 and 346° respectively.

The fact that some halogen derivatives, as $SbCl_5$, $TiCl_4$, VCl_4, &c., melt at temperatures below 0°, and that other derivatives, as $SbCl_3$, $SnCl_4$, CrO_2Cl_2, $TiCl_4$, and $WOCl_4$, boil at temperatures not far removed from 200°, shows that some metallic compounds exist which, in the liquid state, have molecular weights expressed by their ordinarily received formulæ, and are therefore strictly comparable with most non-metallic inorganic compounds. When, however, we examine the derivatives of most other metals we find a far different state of things to obtain. Thus the halogen derivatives of silver, thallium, and lead melt at about 400—500°, and boil at much higher temperatures, whilst if they consisted of simple molecules they should melt below 0°. Their molecules in the liquid state can thus scarcely consist of less than four or eight ordinary molecules. Again, the derivatives of the metals of the alkalis and alkaline earths only melt at about 700°, whilst their boiling-points are so high that they have not been determined ; their molecules in the liquid state must therefore be still more complicated. What is true of these halogen derivatives may be applied equally to almost all the oxides and most other salts of the metals. Thus ruthenium and osmium tetroxides, chromium trioxide, and perhaps manganese heptoxide, are the only oxides which melt at temperatures below 200°, and of these OsO_4 and RuO_4 are the only ones which can be volatilised without decomposition. Most oxides do not even fuse at the highest temperature of the oxyhydrogen flame, so their molecules are in all probability exceedingly complex. Most other salts when exposed to high temperatures decompose without previous fusion, so it can only be concluded that their molecules are complex, without it being possible to say whether they are as complex as oxides.

The instances of abnormal boiling-points among carbon

Chloride.	Boiling-point.	Bromide.	Boiling-point.	Increase of b. pt. per each atom of bromine.
PCl_3 ..	76°	PBr_3 ..	175°	33°
$POCl_3$ ..	107·2	$POBr_3$ ..	195	29·3
$AsCl_3$ ..	134	$AsBr_3$ ..	220	28·7
BCl_3 ..	18·2	BBr_3 ..	90·5	24·1
$SiCl_4$ ..	59·6	$SiBr_4$ ..	154	23·6
$CHCl_3$ ..	61	$CHBr_3$ ..	151	30
CCl_4 ..	76·5	CBr_4 ..	189	28·1
CH_3Cl ..	−22	CH_3Br ..	4·5	26·5
$TiCl_4$ ..	136·1	$TiBr_4$ ..	230	23·5

compounds are very numerous, so only some of the more remarkable of them will be indicated here.

Hydrocyanic acid, boiling at 26·5°, form a well-marked exception. Thus cyanogen itself boils at −20·7°, or 47·2° lower, whilst the hydrogen derivatives of the halogens boil considerably lower than the analogously constituted halogens themselves. Thus chlorine boils at −34°, and hydrochloric acid boils at about −100°, or 66° lower. Bromine boils at 63°, and HBr at −73°, or 136° lower; iodine boils at about 200°, and HI at about −25°, or 225° lower. The effect of the introduction of hydrogen into the halogen molecule is thus less marked the more volatile the halogen. Now cyanogen is less volatile than chlorine, but considerably more so than bromine; it should therefore boil some 76° lower than its hydrogen derivative, or hydrocyanic acid should boil at about −96°. Its real boiling-point is thus some 122° too high. Now tricyanogen chloride, $C_2N_3Cl_3$, boils at 190°, whilst cyanogen chloride boils at 15·5°, or 174·5° lower; also paraldehyd boils at 124°, or 103·2° higher than acetal-dehyd. We may therefore consider liquid hydrocyanic acid as probably the triple compound, especially as it is known that such triple molecules are of ready formation among cyanogen compounds.

It is a matter of doubt whether at temperatures just above their boiling-points aluminium methyl and ethyl have vapour densities corresponding to the formulæ Al_2Me_6 and Al_2Et_6, or to half these formulæ. The boiling-points of these bodies indicate that in the liquid state the higher values obtain. Thus NEt_3 boils at 89°, and PEt_3 at 127°, or 38° higher; CMe_4 boils at 10°, and $SiMe_4$ at 30°, or 20° higher. Boron ethide, BEt_3, boils at 95°; aluminium ethide should therefore boil at about 125°, whilst in reality it boils at 194°, or 69° higher. Also boron methide boils at a temperature not far above 0°; hence aluminium methide, boiling at 130°, has a value abnormal by a rather greater amount than for the ethide. It is evident, therefore, that in the liquid state the molecules of these bodies have the higher values.

We now come to more important exceptions, which, indeed, appear to extend to whole classes of compounds. Thus, from the study of boiling points it will be shown that in all probability all compounds, both organic and inorganic, containing one or more hydroxyl groupings, possess in the liquid state molecular weights double those expressed by their ordinarily received formulæ. Many of the derivatives of amidogen also appear to possess abnormal molecular weights.

To take firstly the organic hydroxyl derivatives, which consist principally of alcohols and acids. The reasons from which the conclusions as to their molecular weights are drawn are as follows :—

(1). The fact that all thio-compounds containing a sulphydryl grouping boil some 30° or more lower than the corresponding hydroxyl compounds, whilst all other thio-compounds not containing a sulphydryl grouping boil some 40° or 50° higher than the corresponding oxy-compounds, which also, of course, contain no hydroxyl groupings.

To prove the validity of this statement, most of the chief thio-compounds are here given, and also the number of degrees their boiling-points are above (+), or below (−), those of the corresponding oxygen compounds.

$(CH_3)_2S$	..	+43°	$CH_3.SH$ ..	−46°	17·5°
$(C_2H_5)_2S$	..	+56	$C_2H_5.SH$ ..	−42·3	56
$(C_3H_7)_2S$	..	+48	$C_3H_7.SH$ ..	−29·4	64
$(C_3H_5)_2S$	..	+55	$C_3H_5.SH$ ..	− 6·5	50
$(C_6H_5)_2S$	..	+40	$C_6H_5.SH$ ..	−15	124
$C_2H_3O.SEt.$		+38	$C_2H_3O.SH$.	−25	28
$CS.NEt$	..	+73	$C_2H_4(SH)_2$.	−51·5	
$CSCl_2$.	..	+62			
$(CH)_4.S$	..	+49			

It would thus seem that, besides the thio-ethers having normal molecular weights, as is shown by the fact of their boiling-points being about 50° higher than those of the corresponding oxygen ethers, the thio-alcohols also have normal molecular weights, and on this account boil at considerably lower temperatures than the corresponding oxygen alcohols, which exist as probably doubled molecules.

(2). The fact that most ethers, both simple and compound, in which the hydrogen of hydroxyl is replaced by a hydrocarbon grouping, boil at temperatures considerably below the boiling-points of the original hydroxyl derivatives, whilst in the case of thio-compounds the opposite is the case, the ethers boiling at temperatures considerably above those of the corresponding sulphydryl derivatives from which they are derived.

In the last column in the above table are given the number of degrees the boiling-points of the thio-ethers are above the boiling-points of their corresponding thio-alcohols or acids. Here it will be noticed that in several cases the ethers boil at 50° or more higher than their corresponding alcohols, and that phenyl sulphide boils as much as 124° higher than thiophenol. The laws as to boiling-points are modified gradually as we pass from compounds containing a lesser to compounds containing a greater number of carbon atoms, so that with these the oxygen ethers begin to have higher boiling-points than their corresponding alcohols. Thus, phenyl ether, $(C_6H_5)_2O$, boils 69° higher than phenol. The difference between the boiling-points of phenyl sulphide and thio-phenol is on this account much greater than the difference for compounds with a lesser number of carbon atoms. Nevertheless it is evident that phenol has a double molecular weight like other hydroxyl derivatives, as it boils higher than its corresponding thio-derivative in the same way that they do.

A few hydroxyl derivatives and their ethers are here given, together with their boiling-points. The last column gives the number of degrees the ethers boil below the hydroxyl derivatives.

Alcohol.	Boiling-point.	Ether.	Boiling-point.	Diff
$CH_3.OH$..	.. 66°	$(CH_3)_2O$..	.. −23°	89°
$C_2H_5.OH$.	.. 78·3	$(C_2H_5)_2O$.	.. 35	43·3
$C_3H_7.OH$.	.. 97·4	$(C_3H_7)_2O$.	.. 86	11·4
$C_3H_5.OH$.	.. 97	$(C_3H_5)_2O$.	.. 85	12
$C_2H_3O.OH$	.. 118	$C_2H_3O.OC_2H_5$	77	41
$C_3H_5O.OH$	.. 140	$C_3H_5O.OC_3H_5$	122	18
$C_4H_7O.OH$	.. 163	$C_4H_7O.OC_4H_7$	157	6

Now it would be naturally expected that the substitution of a hydrocarbon grouping for an atom of hydrogen in any molecule would be attended by a rise of boiling-point, and such was seen to be the case with thio-compounds. Such, indeed, is the case with all compounds but hydroxyl derivatives. Thus the following instances show that the rise in boiling-point, on substitution of hydrogen by a hydrocarbon grouping, is considerable.

Substance.	Boiling-point.	Derivative.	Boiling-point.	Rise in boiling-pt.
$CH_3.CHO$ ..	20·8°	$CH_3.CO.CH_3$ ..	56·5°	35·7°
$CHCl_2.CHO$.	89	$CHCl_2.CO.CH_3$.	120	31
$C_2H_5.CHO$ ..	49	$C_2H_5.CO.CH_3$ ..	81	32
$C_6H_5.CHO$ ..	179	$C_6H_5.CO.CH_3$ ..	200	21
$C_6H_5.NH_2$ ..	183	$C_6H_5.NH.CH_3$..	191	8
$C_4H_4.O$ . ..	35	$C_4H_3(CH_3).O$ ..	63	28
$C_4H_4.S$ . ..	84	$C_4H_3(CH_3).S$ ..	113	29

How, therefore, can it be explained, except on the assumption of the doubling of the molecular weight of hydroxyl derivatives ?

(3). Other groupings besides hydrocarbons, when substituted for the hydrogen of hydroxyl, also lower the boiling-point. Thus, for instance, compound ethers may be considered as alcohols with the hydrogen of hydroxyl replaced by an acid radicle. Now $C_2H_5.OH$ boils at 78·3°, but $C_2H_5O.CHO$, in which hydrogen is replaced by formyl, boils at 54·4°, or 22·1° lower; even the acetyl derivative, $C_2H_5O.C_2H_3O$, boils at 77°, or 1·3° lower.

When, however, the grouping formyl replaces a hydrogen atom in furfuran, the boiling-poing is raised 127°. Again, ethyl nitrite, $C_2H_5O.NO$, boils at 16°, or 62·3° lower than ethyl alcohol; methyl nitrite boils at −12°, or 78° lower than methyl alcohol. Even methyl nitrate, $CH_3O.NO_2$, only boils at 66°, or the same temperature as methyl alcohol; whilst in other cases the substitution of $-NO_2$ in a molecule raises the boiling-point greatly. Thus benzene boils at 80·5°, and nitro-benzene at 205°. Again, methyl borate, $B(OCH_3)_3$, boils at 65°, or 1° lower than methyl alcohol, from which it can be considered as derived by substitution of $B(OCH_3)_2$ for its hydrogen atom.

Lastly, it is noticeable that some organic anhydrides—bodies which have nearly double the molecular weight of the free acids—boil at temperatures but slightly higher than those of these acids. Thus acetic anhydride boils at 137°, or only 19° higher than acetic acid itself.

(4). The complexity of the molecules of a few organic compounds at temperatures above their boiling-points has been proved experimentally by means of vapour density determinations. Thus both formic and acetic acids, at temperatures only slightly above their boiling-points, have molecular weights nearly three times those of their ordinarily received formulæ. It is not probable, however, that in most cases such molecular complexity extends to beyond the solid and liquid states.

(5). If some compound containing hydroxyl, as ethyl alcohol, be compared with other bodies of about the same boiling-point, and also containing an ethyl grouping, it will be rendered evident how very much greater is the molecular weight of these other groupings which go to form the molecule than is that of hydroxyl.

Substance.	Boiling-point.	Molecular weight.
$C_2H_5.OH$	78·3°	46
$C_2H_5.C_4H_9$	71	86
$C_2H_5.CHCl_2$	84	113
$C_2H_5.OC_3H_5$	66	86
$C_2H_5.N(C_2H_5)_2$ . ..	89	101
$C_2H_5.PH(C_2H_5)$. ..	85	90
$C_2H_5.CH_2CHO$ . ..	75	72

These groupings, which from the boiling-points of the bodies produced by combining them with ethyl are comparable with hydroxyl, are, it is evident, quite incomparable from the standpoint of molecular weight. If, however, the molecule of liquid ethyl alcohol be supposed to have double the ordinary molecular weight,—namely, 92 instead of 46,—then it is of a value almost identical with the mean of the molecular weights of the bodies given, viz., 91. It is not, of course, even approximately correct to state that the boiling-point of a body depends only on its molecular weight; but it is scarcely possible that, of a series of bodies of about the same boiling-point, one should have half the molecular weight of any of the others, the molecular weights of all of these being of similar value.

If we examine again the thio-compounds, it will be seen that they also seem to indicate that hydroxyl compounds in the liquid state consist of double molecules, and are not in a higher state of complexity than this. Thus the thio-ethers boil at about 58° higher than the corresponding thio-alcohols. Oxygen ethers should therefore boil about this amount higher than alcohols, whereas they in reality boil about 40° lower. Alcohols, therefore, boil about 100° too high, which is about the increase found to obtain on doubling the molecular weights of the members of the olefine series. On calculating the boiling-points of other bodies as acetic acid in this manner, it is found that the calculated value, though considerably below the actual, is not nearly so much so as for alcohols. It may still be taken, however, to indicate the doubling of the molecule after the same manner as for alcohols; for it is a well-known fact that in many cases the increase of the molecular weight of a body by addition of other groupings is not attended by as great an increase of boiling-point if the body already has a high boiling-point as if it has a low one. Now acids boil some 40° higher than their corresponding alcohols, — so their boiling-points are accordingly not abnormal to so great an extent.

As regards inorganic hydroxyl derivatives, it is probable that they also in the liquid state exist as doubled molecules. There are not, however, so many data to prove this statement as there were for organic derivatives. Thus there are no sulphydryl inorganic compounds to compare with the corresponding hydroxyl compounds, except sulphuretted hydrogen, which has been shown to be very much more volatile than water. Again, there are but two cases in which it is possible to compare the boiling-points of acids and the anhydrides from which they are derived. Nitric acid boils at 86°, and nitric anhydride at 45°, or 41° lower; whilst chlorsulphonic acid,—

$$SO_2\begin{cases} OH \\ Cl \end{cases},$$
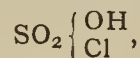
boils at 158°, and disulphuryl chloride, $S_2O_5Cl_2$, at 146°, or 12° lower. Thus in each case the anhydride, though of nearly double formula weight, boils at a considerably lower temperature.

When the hydrogen of hydroxyl of such volatile acids as are known is replaced by a paraffin grouping, the boiling-point is lowered considerably. Thus dimethyl sulphuric ether, $SO_2(OCH_3)_2$, boils at 188°, or 150° lower than sulphuric acid; and the ethyl derivative boils at 208°, or 130° lower. Methyl nitrate boils at 66°, or 20° lower than nitric acid; ethyl nitrate boils at 86°, or the same temperature as the acid from which it is derived. Ethyl perchlorate, $C_2H_5ClO_4$, probably boils at a considerably lower temperature than perchloric acid. Ethyl chlorsulphonate,—

$$SO_2\begin{cases} Cl \\ OC_2H_5 \end{cases},$$
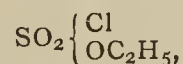
boils at 150°, or 8° lower than chlorsulphonic acid.

As, therefore, the above data show that hydroxyl containing acids in the liquid state have doubled molecular weights, chlorsulphonic acid must exist as a doubled molecule. Now it has previously been shown that the molecules of sulphuric acid are double as large as those of this acid; therefore in the liquid state sulphuric acid probably exists as quadrupled molecules.

Most organic derivates containing amidogen, and many containing imidogen, groupings, appear to possess abnormal molecular weights, but they do not all seem to come under a general law in the same way as hydroxyl derivatives. All monamines and diamines — both primary, secondary, and tertiary—appear to possess normal molecular weights, and, on the other hand, many amidogen derivatives have molecules much more complex than merely doubled ones.

The existence of the amines as simple molecules is rendered evident by the fact of their boiling-points being slightly lower than those of the corresponding phosphorus compounds, whilst these are more volatile than the arsenic derivatives. Thus NH_2Et boils at 18°, and PH_2Et at 25°; NEt_3 boils at 89°, PEt_3 at 127°, and $AsEt_3$ at 140°. On comparing the amines with the corresponding halogen derivatives, it is found that a hydrocarbon grouping, combined with one or two amidogen groupings, has a boiling-point higher than the corresponding mono- or dichlor-derivatives, but lower than the bromo-derivatives. Thus EtCl boils at 12·5° and EtBr at 39°, $EtNH_2$ boiling at 18°. $C_2H_4Cl_2$ boils at 84° and $C_2H_4Br_2$ at 131°, whilst $C_2H_4(NH_2)_2$ boils at 123°. We have thus some sort of guide as to what the boiling-points of amidogen compounds should theoretically be by mere observation of the boiling-points of the corresponding halogen derivatives, for these have always been found to be normal. Acetyl chloride boils at 55°, the bromide at 81°; acetamide should therefore boil below 70°; in reality it boils at 222°,

or some 150° too high. Even diacetamide, $(C_2H_3O)_2NH$, only boils at about 212°. The acetamide molecule must accordingly, in the liquid state, be at least doubled, and probably trebled. The same arguments apply equally to the other amides of the fatty acids.

Glycocoll, $CH_2NH_2.COOH$, is not at all volatile, and indeed only melts at about 234°. The corresponding chlor- and brom-acetic acids, which, being hydroxyl derivatives, must have double molecular weights, boil at 186° and 208° respectively. The ethyl ester boils at 149°, and is therefore normal. These data show that the glycocoll molecule must be very complex, containing at least four, and probably more, ordinary molecules. The other amido acids and their derivatives are equally unvolatile, so their molecules must also be considered complex. Some of the derivatives of urea probably exist as doubled molecules. Thus the body $CO(NEt_2)_2$ boils at 212°, or considerably lower than $CO(NHEt)_2$, which boils at 263°. Succinimide boiling at 288° seems normal, as this value is but slightly higher than for succinic anhydride, which boils at 250°. Pyrrol, C_4H_4NH, however, appears to be abnormal, as it boils at 131°, whilst pyridine, C_5H_5N, only boils at 117°. Also the methyl derivative of pyrrol, $C_4H_4NCH_3$, boils at 113°, or 18° lower than pyrrol itself, whilst the isomeric derivative, $C_4H_3CH_3.NH$, boils at 148°, or 17° higher. It is therefore probable that pyrrol itself exists as a double molecule, but that the derivative, $C_4H_4.NCH_3$, which does not contain an imidogen grouping, exists as a simple molecule.

It seems probable that aniline has an abnormal molecular weight. Thus it has been shown that the phosphines boil higher than the amines, but the body $C_6H_5.PH_2$ boils at 160°, or 23° lower than aniline: also $(C_6H_5)_2PH$ boils at 280°, or 30° lower than $(C_6H_5)_2NH$. As $C_2H_5NH_2$ boils 7° lower than $C_2H_5PH_2$, aniline boils about 30° too high. Again, nitroethane, $C_2H_5NO_2$, boils 96° higher than ethylamine, so, as nitrobenzene boils at 205°, aniline should boil at about 109°, instead of 183°. Still again, monochlorbenzene boils at 132° and mono-brombenzene at 155°, so aniline should boil at about 140°.

It will be seen that the subject of the molecular weights of amidogen derivatives is much more complicated than that of other classes of organic compounds. Only a few of the chief compounds have therefore been dwelt upon, as an exhaustive study of the whole class of these derivatives would be far beyond the limits of this paper.

We have thus seen that, by studying and comparing the boiling-points of compounds, it is possible, in a large number of cases, to determine with a considerable degree of probability the state in which the liquid molecules of these bodies exist. The subject has not been dealt with as thoroughly and exhaustively as it might have been; but the object of this paper was rather to indicate a method by which some sort of results might be obtained, so as to show that a careful study of the whole of the different classes of compounds, both organic and inorganic, with reference to their boiling-points, would not be without profit. The chief objection to the method is that the results obtained cannot be formulated with exactness, but can only be expressed in probabilities. It is likely, however, that with further study of the subject it will be possible to speak with greater certainty. Even if this is not so, the results may be considered to have a certain amount of value, as apparently no other method has yet been brought forward whereby the molecular weight of a liquid body, undissolved in any other liquid, is attempted to be determined.

Influence of Fluorides upon the Growth of Yeast. —J. Effront.—Small additions of ammonium fluoride were found unfavourable to the increase of yeast, but gave nevertheless good results as regards the yield of alcohol. —*Bull. de la Soc. Chim. de Paris*, v., No. 10.

INDIGO-GREEN: A COLOURING-MATTER OBTAINED FROM SULPHINDIGOTIC ACID.

By V. H. SOXHLET.

DURING the examination of various indigo extracts (indigo carmine, sodium sulphindigotate), to determine their market value, by a strange oversight a considerable quantity of liquid ammonia was poured into a glass containing indigo-carmine. The glass was stoppered, set aside, and left to itself. After about ten days it was again taken up, when, on the point of having it cleared out, I perceived that the colour of the liquid had changed from a deep blue to a yellowish green. This was the origin of the present communication.

On a superficial examination of the yellowish green liquid, it appeared that several colouring-matters must be present, for, although of a very intense yellow, if slightly sprinkled upon white filter-paper, it showed shades varying from the deepest dark blue to the palest straw-yellow. Hence it was doubtful if the observation could be made available for practical purposes. The only similar substance which I found described was the sulphoviridic acid of Berzelius. This compound was obtained by evaporating to dryness a solution of barium sulphindigotate, precipitating the re-dissolved barium salt with basic lead acetate, and decomposing with sulphuretted hydrogen. Sulphoviridic acid, however, though it is a green dye-ware, is soluble only in absolute alcohol, and has consequently met with no technical application.

I began my experiments in a regular manner, weighing out equal parts of indigo extract, and mixing them with liquid ammonia (sp. gr. 0·936) in increasing proportions, as 1 : 1, 1 : 2, 1 : 3, and 1 : 5, stopping the glasses well and letting them stand for eight to ten days.

On examination at the end of this time it appeared that the specimens which had received the largest additions of ammonia displayed the finest green colours, whilst specimens which had been mixed only with equal or double weights of ammonia showed a dark bluish green. We may assume that, even on using only equal parts of indigo-carmine and ammonia, corresponding results would be obtained if the action were sufficiently prolonged. It is easy to understand that the acidity of the indigo-carmine, or the indigo extract, will play here an important part.

It was not to be expected that the green dye-ware, in its alkaline state, would be able to dye wool, as I soon convinced myself by a small experiment. One specimen of the green solution of indigo was mixed with dilute sulphuric acid until the mixture had a faintly acid reaction. I then added a solution of sodium chloride of the strength of 14° Tw., stirred it up well, and filtered it through felt. The feebly acid filtrate had a light green colour, but was red by reflected light—a further analogy with the sulphoviridic acid of Berzelius. The paste obtained had the appearance of commercial indigo-carmine, but without its coppery lustre. It was easily soluble in warm water. White yarns took on, in the hot solution, a shade closely resembling that of methyl-green, and which retains the green colour by gas- or candle-light.

The operation of dyeing went on normally; the colour took upon the fibre more evenly than indigo preparations do; the fastness against light is equal to that of indigo extracts. Its fastness against washing, alkalies, &c., is decidedly better. Experiments on the large scale have not yet been made with this dye, as I wish to determine the method of manufacture more precisely.

In experiments on preparing the indigo-green on a larger scale I used the commercial dry extract, such as it is chiefly made and used in England. It has certain advantages as compared with the paste, since it is more easily mixed with the ammonia, and generally contains less free acid than the semi-fluid paste.

On more prolonged action of ammonia upon indigo

extract no essential difference could be detected in the dyed shades, though the original ammoniacal liquid had decidedly a more yellow colour. Even when the ammoniacal solution of indigo had become a yellowish brown, on neutralising it with sulphuric acid a green was always obtained on the fibres.

Further experiments, to treat potassium sulphindigotate with ammonium carbonate under pressure had a negative result. If a solution of indigo extract is treated with liquid ammonia and caustic soda-lye a yellow colouration rapidly appears. But this product will scarcely admit of practical applications, as it dyes up only dirty shades on wool and silk.

The author's indigo-green consists at least of two colouring-matters, which dye respectively yellow and green.—*Chemiker Zeitung*.

NOTICES OF BOOKS.

The Organic Elements and their Position in the System. An Address delivered before the German Chemical Society at Berlin, on March 23rd, 1891. (Die Organischen Elemente und ihre Stellung im System. Ein Vortrag gehalten in der Deutschen Chemischen Gezellschaft zu Berlin, am 23ten Maerz, 1891). By W. PREYER. Wiesbaden: J. F. Bergmann (8vo., pp. 47).

PROF. PREYER undertakes here an arduous and a twofold task. He seeks, as do not a few of the more philosophical men of science of the day, to introduce the concept of evolution into general chemistry, though he admits it will only attain recognition after a long time. He at the same time raises the difficult question why only certain elements, to the exclusion of others, play a necessary part in the maintenance of life upon our earth? As such he acknowledges only fourteen, all of which have atomic weights lower than 56. His organic elements are hydrogen, carbon, nitrogen (which our French neighbours ought to have called "zote" instead of azote), oxygen, fluorine, sodium, magnesium, silicon, phosphorus, sulphur, chlorine, potassium, calcium, and iron. Here, already, there is room for discussion. How are we to exclude copper from the list? It is found in vegetable products of various kinds, grown upon the soils of different geological formations, and more especially in the cacao-nut. We do not mean in the cocoa or chocolate of commerce, where it might possibly have been introduced by the instruments or ingredients used in the manufacture, but in the nuts as plucked from the tree.

There are cases in which copper appears to be not merely absorbed by animals, but assimilated. Harlen detected copper in the blood and in the liver of certain mollusks, especially cephalopods. His experiments indicate that in them this element "stands in an essential relation to the blood-corpuscles." In the blood of the cephalopods there has been detected an organic copper compound, known as hæmocyanine, which fulfils the functions due in the higher animals to hæmoglobine.

Von Bibra detected copper in certain crustaceans, such as *Cancer pagurus*, and found that it occurred in an inverse ratio to the iron, which it more or less completely replaced. Dr. Genth quantitatively determined the copper in the blood of the *Limulus*, a crab found on the coasts of North America. The blood of the healthy females, just before laying their eggs, was of a rich blue, and when dried the incinerated residue contained 0·295 per cent of copper oxide and but a mere trace of iron oxide. Surely these observations should be proved erroneous before copper is deleted from the list of organic elements.

In like manner Prof. Preyer thinks it "not improbable that those oceanic plants and animals in which iodine and bromine are regularly found would flourish as well in waters in which these elements are wanting." The only answer to this question is experimental. If anyone can find plants or animals of the same species which otherwise contain iodine or bromine, living and increasing in the absence of these halogens, the author's argument—which is merely an assertion of non-improbability—holds good. But until such *à posteriori* evidence is produced it cannot be accepted.

The argument that the number of organic elements cannot exceed fourteen, because the milk of the highest animals contains no more, is not trustworthy. We have no proof that additional elements are not present in the Articulata, in the Mollusca, or in plants. Iodine, bromine, copper, may be eliminated in the progress of higher development.

Prof. Preyer, in concert with Dr. Wendt, endeavours to lay down, *à priori*, the number of possible elements of which our earth—or rather its upper strata—may consist. He holds that their number must be at the utmost 91, and at the lowest 84, of which 68 are already known. Here, again, we should prefer to leave the question open, and await the results of spectroscopic and micro-chemical analysis.

But whilst a certain portion of Prof. Preyer's researches must, for the present at least, be entered in a "suspense account," his labours in extending the great principle of evolution to the chemical elements deserve the fullest recognition. We find here a quotation from Prof. Kekulé which has not received the attention it merits:—"The relations of a body to that which it once was, and to that which it may become, form the essential object of chemistry."

The late regretted Clemens Winkler—too early lost to Science — declared his conviction that the chemical elements have arisen from "more simple matter," "from a primal matter" (protyle), "unknown to us and engaged in a gradually progressing condensation."

If the chemical elements have neither been created nor developed from some primary material, — both which origins Prof. Mendeleeff denies,—how can we possibly account for the relations which exist between them? Such relations seem to us absolutely unthinkable among a set of bodies which have come into existence at haphazard, or equally by chance have existed in the universe from all eternity.

CORRESPONDENCE.

A CASE OF META-CHEMISTRY.

To the Editor of the Chemical News.

SIR,—In a paper on "Destructive Distillation" which Dr. Mills has published in the June number of the *Journal of the Society of Chemical Industry*, he brings forth fresh evidence in favour of his pet theory (see same Journal, year 1885. p. 325) that, in things like coal, shale, &c., "the distribution of the original material is based upon a C_3 unit."

A Scottish bituminous coal, bearing the jaw-breaking name of "Balquhatstone," was analysed and found to contain—

Carbon	82·54 ⎫	
Hydrogen	4·88 ⎬ 93·00	
Oxygen	5·58 ⎭	
"Pit Water" ..	2·52	
Nitrogen	1·75	
Sulphur	0·77	
Ash	1·96	
	100·00	

From these numbers Dr. Mills concludes that the "carbon, hydrogen, and oxygen have the relation $C_{18}H_{12}O$," and then, referring to his book on "Destruc-

tive Distillation " (pp. 39, 40, 56), compares this formula with others similarly worked out :—

Yorkshire and Durham	$C_{24}H_{18}O$
Balquhatstone	$C_{18}H_{12}O$
Boghead	$C_{12}H_{20}O$
Average Cannel	$C_{12}H_{12}O$
Heywood Gas Cannel	$C_9H_{12}O$
Good average Scotch Shale	$C_6H_{10}O$

But what do these formulæ prove ? Why, any person who, besides being a chemist (I mean one of the ortho- or at least of the para-kind), is not utterly devoid of the faculty of arithmetical reasoning, will simply laugh at these meta-chemical exercises. In the present case, indeed, the results of the analysis agree far better with the formula $C_{20}H_{14}O$ than with Dr. Mills's own, as seen by the following comparative statement :—

	Found.	Demanded by	
		$C_{18}H_{12}O.$	$C_{20}H_{14}O.$
Carbon	88·76	88·53	88·89
Hydrogen	5·25	4·91	5·19
Oxygen	6·00	6·56	5·92
	100·00	100·00	100·00

In a similar manner small-integer formulæ, *not* " based upon a C_3 unit," might be calculated for the Yorkshire, Boghead, Average Cannel, &c , but it is not worth while to do so ; I prefer to confidently give it as my opinion that all Dr. Mills's formulæ—inasmuch as they pretend to do more than symbolise the direct results of the respective analyses—are just meta-chemistry pure and unmixed, or, to put it into plainer English, unmitigated ———. The same remark is a sufficient critique of Dr. Mills's monstrous equations to explain the re-distribution of carbon, &c., which takes place when that " Balquhatstone" (I hope I have spelled it correctly) is subjected to dry distillation at low temperatures and high temperatures respectively. For the benefit of those of your readers, however, who have not the *Soc. Chem. Ind. Journal* at hand, I will reproduce the low-temperature equation as a specimen :—

$$28C_{18}H_{12}O = C_{444}H_{123} + C_{30}H_{76}O_9 + C_{30}H_{105}O_3 + 16H_2O.$$
$$\text{Coke.} \qquad \text{Tar.} \qquad \text{Gas.} \qquad \text{Water.}$$
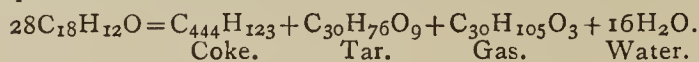
In a similar manner one might, in reference to the cooking of a steak, formulate the relation between the several portions of carbon, hydrogen, and oxygen which pass into the cooked steak, the gravy, and the chimney respectively! And thereby render an additional service to——Meta-Chemistry.—I write in the name of

COMMON SENSE.

July 25, 1891.

THE INSTITUTE OF CHEMISTRY.

To the Editor of the Chemical News.

SIR,—I was a competitor in the recent examination of candidates for the Associateship of the Institute of Chemistry. The general arrangements gave great dissatisfaction to the majority of the examinees, and I am curious to learn if members of the Institute consider an examination so conducted a test of the capabilities of the competitors.

At the London centre fifteen candidates presented themselves. Three balances only were provided, and one of these was in bad working order ; the balance cases were devoid of drying material, and no proper weighing tubes or watch-glasses were obtainable. There was but one sulphuretted hydrogen Kipp in the laboratory, and no solution of the gas. The benches were unprovided with most necessary reagents, and even the concentrated mineral acids had to be taken as required from large stock bottles at one end of the room. The utensils and apparatus provided were quite inadequate for the proper performance of the work set, and candidates were com-

pelled in consequence to resort to obsolete and unreliable methods.

I am convinced that no one could obtain reliable results under such conditions, and that it would be practically impossible to discriminate between the good and bad workers It seems probable that inferior men may be admitted as Associates in consequence, and possibly good men rejected. I should like to know from any of your readers if this examination is generally regarded as a fair test, and if so, whether it has not this year degenerated from the usual standard.—I am, &c.,

ZERO.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxiii., No. 2, July 13, 1891.

A Contribution to the Study of so-called " Natural Meadows."—A. Chatin.—The author defines natural meadows as those composed chiefly of plants belonging to the family of the Gramineæ, whilst artificial meadows are composed of leguminous plants, lucerne, clovers, sainfoin, and medicago.

On the Cyanalkoylic, Cyanobenzoylic, and Cyanorthotoluylic Camphors. — A. Haller.—The author's researches prove that camphor contains a group—

$$\left\langle\begin{array}{c} CH_2 \\ | \\ CO \end{array}\right.,$$

as Kekulé's formula requires. A further proof of the presence of this arrangement of atoms is the property which camphor possesses of giving rise to the isonitro-camphor of Claisen and Manasse.

On a New Copper Hydride and on the Preparation of Pure Nitrogen.—A. Léduc.—The new compound has nothing in common with the compound discovered by Wurtz, which is formed in the cold and destroyed entirely about 60°. Léduc's hydride is produced at a dull red heat by the direct union of its elements, and presents mere traces of dissociation at a cherry-red heat. It is a body of a fine hyacinth red, which covers the metal. It appears certain that the hydrogen is really combined with and not dissolved in the metal. The author considers it interesting to resume the study of the decomposition of gaseous ammonia by metals and especially by copper.

Action of Light upon Silver Chloride.—M. Guntz. —On exposing AgCl to light in a thin layer upon a plate of glass, it is in the first moments only coloured very slightly, but if it is then placed in the solution of iron oxalate the silver chloride is reduced, with a formation of metallic silver. Even in the absence of light the author has succeeded in producing a modification of silver chloride which is directly reduced by the oxalate solution. To obtain this modification it is merely necessary to boil silver chloride for some hours in the absence of light. If, on the contrary, silver chloride is left for some time exposed to the light it takes a violet-red tint and loses chlorine. The silver sub-chloride formed on prolonged exposure to light yields, on further reduction, metallic silver. A layer of silver chloride after exposure to light consists of three superimposed layers, metallic silver, silver subchloride, and unaltered AgCl.

On a New Gaseous Compound : Phosphorus Pentafluochloride. — C. Poulenc. — The compound in question, PF_3Cl_2, is a colourless gas, possessing an irritating odour, not combustible in the air, and instantly

absorbed, with decomposition by boiled water. Alkaline solutions, lime-water, and baryta-water, absorb it. Its density, as determined by Chancel's apparatus, is 5·40, the theoretical density being 5·46. At common pressures it is liquefied at a temperature bordering upon −8°. At 250° it is decomposed, yielding gaseous phosphorus pentafluoride and solid phosphorous pentachloride. At 115° sulphur reacts upon phosphorus pentafluochloride, yielding sulphur chloride and a new gaseous compound, phosphorus sulphofluoride. This gas has a peculiar offensive odour, it is rapidly absorbed by an alkaline solution, and is split up in contact with water, yielding hydrofluoric acid, phosphoric acid, and hydrogen sulphide. Ammonia combines at common temperatures with phosphorus pentafluochloride, forming fluorophosphamide—a white, light solid, soluble in water.

Combination of Boron Bromide with Hydrogen Phosphide. Boron Phosphide.—A. Besson.—Boron bromide absorbs hydrogen phosphide at common temperatures, forming a very light amorphous solid, which fumes and ignites spontaneously on exposure to the air. It can be examined only in an atmosphere of carbon dioxide perfectly dry. Its composition is shown by the formula BBr_3PH_3. Boron phosphide, PB, is a brown solid, insoluble in water, soluble in concentrated boiling alkalis, with formation of hydrogen phosphide. Monohydrated nitric acid decomposes it with brisk incandescence; dilute nitric acid decomposes it violently. It burns in the cold if thrown into chlorine gas.

Researches on the Alkaline Earthy Zirconates.—L. Ouvrard. — The author has obtained the calcium, strontium, and barium zirconates. His researches establish an additional analogy between zirconium, tin, and titanium.

Artificial Production of Datholite.—A. de Gramont. —This paper does not present any chemical interest.

Action of Boron Fluoride on the Nitriles.—G· Patein.—Boron fluoride combines in definite proportions, molecule to molecule, with the nitriles both of the fatty and the aromatic series.

On the Acid Sulphated Ferrugino-Aluminic Waters of the District of Rennes-les-Bains (Arde). —Ed. Willm.—This memoir, though placed under the heading "analytical chemistry," does not describe any new or improved analytical process, but merely gives the composition of certain mineral waters.

On the Formation and Oxidation of Nitriles during Nitrification.—S. Winogradski.—In a number of experiments made with soils from different countries, nitrification always began with the formation of nitrous acid, which rapidly increases in quantity. When the ammonia present in the "culture" had disappeared, the nitrite formed was oxidised and very rapidly converted into nitrate. The exotic nitric ferments isolated were without action upon ammonia.

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Bulletin de la Société Chimique de Paris.
Series 3, Vol. v., No. 10.

On Levosine, a New Proximate Principle of some Cereals. — C. Tanret. — Anhydrous levosine may be represented by the formula $C_{48}H_{40}O_{40}$. It is a white amorphous body, almost tasteless. It is very soluble in water in all proportions, and dissolves freely in weak alcohol, but scarcely in alcohol at 95°. It does not reduce Fehling's liquid, and does not ferment with beer-yeast. Diastase—whether obtained from malt, from bran, or from saliva—has no action upon levosine.

On a Crystalline Compound of Absolute Alcohol and Sodium Disulphide.—L. Dumont.—The compound in question has the composition $C_4H_6O_2 + 9(NaS_2)$. If placed in a dry desiccator, at the ordinary pressure, it is converted into a mixture of sodium thiosulphite and sulphite and a little sulphur.

Action of Benzyl Chloride upon Orthotoluidin.— Ch. Rabaut.—The product of this reaction is an oil of a pale yellow colour, which appears to be benzyl orthotoluidin, and is composed of 84·49 per cent carbon, 8·02 of hydrogen, and 7·48 nitrogen.

Determination of Acetone in Denatured Alcohols. — Leo Vignon. — The determination of acetone is effected by utilising Lieben's reaction, which consists in transforming acetone into iodiform by the simultaneous action of iodine and soda. The author operates in the following manner :—After having sought for aldehyd, and eliminated it if needful, according to the indications of Bardy, he takes 5 c.c., which are made up to 250 c.c. with distilled water (A). In a test-glass having a foot, graduated to 100 c.c. and fitted with a ground stopper, he introduces 10 c.c. of binormal soda [(2NaOH in grms. = 1 litre)] and 5 c.c. of the mixture A. After shaking up there are poured into the glass 5 c.c. of binormal iodine [(2I + 2KI) in grms. = 1 litre), and the whole is shaken up again ; the iodine liberated is dissolved by the addition of 5 c.c. of ether. On weighing the residue from the evaporation of 5 c.c. of ether, under known conditions, the quantity of acetone is known. But the result must never be accepted as final until it is confirmed by a determination effected with a double quantity of iodine and soda.

Pump which is Automatically Re-filled with Mercury by means of the Water Pump.—A. Verneuil.— This paper requires the accompanying figure.

Composition of the Brandies and Alcohols of Commerce. — Ed. Mohler. — The author expresses the acids as acetic acid, after determination with decinormal potassa. The ethers are expressed as ethyl acetate, and determined by saponification with decinormal potassa. The aldehyds are expressed as ethylic aldehyd, and determined colorimetrically after treatment with rosaniline bisulphite by comparison with a type-solution of aldehyd at 1-20,000. The higher alcohols are expressed as isobutylic alcohol (or amylic alcohol in case of industrial alcohols), and determined by the colour reaction of sulphuric acid upon alcohol freed from aldehyds by means of aniline diphosphate and a colorimetric comparison with a type solution of amylic or isobutylic alcohol at 1-5000. The nitrogenous products are estimated as ammonia.

Remarks on the Phenomenon of Coagulation : Fibrine and the Coagulation of the Blood. — A. Béchamp.—The author absolutely distinguishes between the coagulation of milk and that of blood. He maintains that fibrine is not a proximate principle, but a mixture formed by a special albumenoid matter inclosing microzymes of a peculiar kind.

Reply to M. Le Bel concerning the Criticism of the foregoing Communication. — A. Béchamp. — A controversial paper, for which we must refer to the original.

Action of Hydroxylamine upon the Acetonic Nitriles.—M. Hanriot.—Not suitable for abridgment.

Vol. v., No. 12.

The Basic Magnesium and Zinc Chromites, and Neutral Cadmium Chromite.—G. Viard.—The object of the present research is to show that magnesium and zinc can yield basic chromites, whilst cadmium under the same circumstances only yields a neutral chromite.

On Turpentine.—Raoul Varet.—Aluminium chloride polymerises the essential oil of turpentine, whilst there is at the same time a formation of cymene, colophene, and other carbides, though in smaller quantities. Turpentine, under the influence of bromine and aluminium chloride, is not split up into isopropyl bromide and a bromo-derivative of toluene.

The Use of the Calorimetric Bomb for Determining the Combustion-heat of Coal. — Scheurer-Kestner.—The use of the calorimetric bomb has constantly yielded lower results than those of the old

calorimeter of Favre and Silbermann. The differences generally lie between 100 and 200 calories. The author thinks that the bomb is more trustworthy, and that its indications should be preferred.

Journal fur Praktische Chemie.
New Series, Vol. xliii., Parts 9 and 10.

On the Naphthoïc Acids.—A. G. Ekstrand. (Conclusion).—Experiments on nitrition with β-naphthoïc acid have very complicated results, since there are formed several—probably five—mononitro-acids, the separation of which is by no means perfect. In the β-naphthoïc acid, as in the corresponding α-compound, the nitro-group is found introduced by preference into the α position of the benzene nucleus. The nitro-β-naphthoïc acids are very similar in their constitution and their properties. the remaining three mononitro-derivatives are formed only in subordinate quantities.

Researches from the Laboratory of A. Weddige. —These comprise a memoir by E. Zacharias on the action of ammonia upon substituted ortho-amido-benzoic ether, and a paper by V. P. Thieme on the action of ammonia and methylamine upon nitrised oxybenzoic ether.

Researches from the Laboratory of the University of Freiburg.— The continuation (Section lxxxvi.) of a treatise on ortho-para-dinitrophenyl and nitroazo- or nitro-nitrosoazo-para chlorophenyl hydrazin and their derivatives.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. vi., No. 63.

This issue does not contain any chemical matter.

Vol. vi., No. 65.

Industrial Production of Lactic Acid. — Georges Jacquemin.—The author prepares a saccharine fermentable wort from malt, introduces pure lactic ferment produced by the method of Pasteur, as also a quantity of pure, sterilised calcium carbonate, and allows the mixture to ferment at 40° to 45°. The fermentation lasts five or six days. The fermented liquid is filtered and evaporated, when an inodorous calcium lactate crystallises out.

Revue Universelle des Mines et de la Metallurgie.
Series 3, Vol. xiv., No. 4.

This issue contains no chemical papers.

MISCELLANEOUS.

British Institute of Preventive Medicine.— Sir Michael Hicks-Beach, who previously gave a negative answer to the request made by the Executive Committee of the British Institute of Preventive Medicine, having reconsidered his decision, has now granted the required license to register the Institution as a Limited Liability Company, with the omission of the word "Limited." The license, however, is not to be construed as expressing approval by the President of the Board of Trade of experiments on animals, or in any way effecting the exercise by the Secretary of State of his discretionary powers to grant a vivisection license to the proposed Institute. The articles of association have been signed, and the Institute is now duly registered. The following gentlemen have already expressed their willingness to serve on the Council :—Sir Joseph Lister (Chairman), Sir Charles A. Cameron, Mr. Watson Cheyne, Prof. Michael Foster, Prof. Greenfield, Prof. Victor Horsley, Sir Wm. Roberts, Sir Henry Roscoe, Prof. Roy, Prof. Burdon Sanderson, Dr. Pye-Smith, and Dr. Armand Ruffer, of 19, Iddesleigh Mansions, Westminster, S.W., will act as hon. sec. until the first meeting of the Council.—19, Iddesleigh Mansions, Westminster, July 29, 1891,

THE CHEMICAL NEWS

Vol. LXIV., No. 1654

THE CONSTITUTION OF THE LIGNO-CELLULOSES.

By C. F. CROSS and E. J. BEVAN.

I.—*Recent Investigations of Soluble Products of Wood Boiling (Bisulphite Cellulose Process).*

THROUGH the kindness of our friend Prof. Tollens, we have received an early copy of the *Inaugural Dissertation* (Gottingen, 1891), of J. B. Lindsey, embodying the results of an extended investigation of the products of the now widely-known " bisulphite " process of treating wood for converting it into a paper-maker's pulp (cellulose). The object of the author, working under the guidance of Prof. Tollens, was to throw light on the constitution of the substance of fir-wood, and the results obtained appear to us to deserve to be promoted without delay from the academic atmosphere in which they first see the light to the " open air " of " working chemistry." We will therefore give a brief abstract of these results, noting subsequently the points in which the author has been able to develop the main subject of his inquiry, viz., the constitution of the lignone, or *non-cellulose* constituent of the wood substance (ligno-cellulose).

This is converted by the process of digestion (at 108° C. — Mitscherlich process) into a soluble derivative, probably, as the author premises, with the minimum of change, and the first part of the work is therefore devoted to the investigation of the waste liquors of this process, holding in solution 9—10 per cent of " total solids." Of these the inorganic constituents are mainly calcium sulphate and sulphite. In the organic constituents the author found small quantities of pentaglucoses, probably xylose, and of galactose or galactan, traces of vanillin, and some quantity of mannose. But by far the larger proportion, say 90—95 per cent, the author finds to be made up of the amorphous or gummy solid which characterises the residue of evaporation. This compound was isolated in a variety of forms, showing a satisfactory uniformity in empirical composition. Of these we may cite the following, omitting the details of the preliminary purification :—

(*a*) Precipitated by alcohol . ..		$C_{24}H_{24}(CH_3)_2SO_{12}$
(*b*) Gums precipitated as lead compounds . {	(1)	$C_{24}H_{24}(CH_3)_2 \cdot SO_{12}$
	(2)	$C_{24}H_{24}(CH_3)_2SO_{12} \cdot 1\frac{1}{2}H_2O$
(*c*) Precipitated by HCl		$C_{24}H_{24}(CH_3)_2SO_{10}$
(*d*) Precipitated by Br		$C_{24}H_{22}(CH_3)_2Br_4SO_{11}$

These bodies may be regarded as derived from the compound $C_{24}H_{24}(CH_3)_2O_{12}$, which is therefore well established, subject to the conditions premised, as *the empirical formula for the lignone constituent of fir-wood.*

The insoluble product of the manufacturing process, *i.e.*, sulphite cellulose, was found to be partially converted into dextrose by treatment with concentrated sulphuric acid. By the action of strong nitric acid this cellulose, and also the original wood, was converted into an oxycellulose, having the empirical composition :—

C	..	.. ..	43·41
H	..	.. ..	6·19
O	..	.. ..	50·40

Similar therefore in composition, as it was found to be

in its properties, with that obtained by ourselves from cotton (*Chem. Soc. Jour.*, 1883).

Such is a brief outline of the author's results, and upon them we offer one or two comments.

The empirical formula deduced by ourselves for the lignone constituent of jute, from the study of its chlorination products (*Chem. Soc. Jour.*, 1889, 213), was $C_{76}H_{80}O_{37}$, which differs but little from Lindsey's formula (*supra*) for the non-cellulose of firwood; for $3 \times C_{26}H_{30}O_{12} = C_{78}H_{90}O_{36}$.

The proportion of methyl groups in the above formula was determined by the hydriodic acid method; they are therefore present as $O \cdot CH_3$ groups. In our paper on the " Constitution of the Jute Fibre Substance " (*loc. cit.*), we noted the formation of acetic acid by the solution of the fibre in sulphuric acid, and deduced from the observation that the CH_3 groups were in union with CO groups. Both conclusions may be true, and would appear to be justified by the study of the products of destructive distillation, of which both $CH_3 \cdot CO$ and $O \cdot CH_3$ groups are prominently characteristic.[*]

The author does not appear to have attempted to diagnose the mode of union of the S atom in the molecule of the derivative of the lignone. It is important, however, to have established the fact of its presence in combination; and it will no doubt prove to have an important bearing on the theory of this process of cellulose isolation. We are engaged, on the other hand, in studying the derivative obtained in the sulphurous acid (Pictet) process of resolving pine-wood, which is of an obviously simpler character, and appears to yield a derivative more closely related to the original lignone than that investigated by Lindsey and Tollens.

Lastly we note that the authors retain the term *lignin* for the non-cellulose constituent of the ligno-cellulose; seeing that the characteristics of the body are those of a ketone, we have suggested the substitution of the term *lignone*, which we think preferable.

II.—*Oxidation of Ligno-Celluloses by Chromic Acid.*

In our earlier contributions to the chemistry of cellulose (CHEMICAL NEWS, xlii., 77; *Chem. Soc. Jour.*, xxxviii., 666) we noticed that the cellulose, isolated by the chlorination method was not homogeneous, containing a form of cellulose easily hydrolysed by acids and alkalies to soluble derivatives; further, that by suppressing or limiting as far as possible the conditions tending to hydrolysis in the process of separating the cellulose, the proportion obtainable, *i.e.*, percentage yield on the raw fibre, could be considerably increased.

Thus, by preventing the rise of temperature in chlorination, and digesting subsequently in aqueous sulphurous acid at 0°, the yield was increased to 80—82 per cent from the 74—76 per cent obtainable without these precautions.

These observations led us to the conclusion—which we give in the words of our first paper (1880)—that " as the cellulose is not homogeneous, and the percentage yield varies with the several methods by which the intercellular substances may be removed, we have reason for believing them to contain a body allied to cellulose. The facts are explained by the hypothesis that the intercellular substance consists of a complicated quinone which is intimately associated with a carbohydrate . . . . more closely allied to cellulose than to glucose."

This view we are now in a position to confirm and develop from results which we have recently obtained by graduated oxidations of the ligno-celluloses with chromic acid. Of these we take the opportunity of giving a brief preliminary notice.

Chromic acid, in cold dilute aqueous solution, is not de-oxidised to Cr_2O_3 by the jute fibre substance; there appears, on the other hand, to be a direct combination and a considerable quantity of the oxide appears to be fixed,

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[*] We also obtain methyl chloride by the destructive distillation of the chlorinated derivative of the lignone of jute.

probably, in part at least, in the form of the oxides intermediate between CrO_3 and Cr_2O_3.

The addition of a mineral acid determines the deoxidation, and the fibre is converted into a greenish product, brittle and yet soft to the touch, and of high lustre. Of this product we obtain from 85—90 per cent of the weight of the raw fibre; in this case a jute of medium quality, yielding about 74 per cent cellulose by the ordinary chlorination method. On ignition it gives an ash containing Cr_2O_3, equal to from 2—2·5 per cent of its weight. The organic portion we find to be an _oxycellulose._ The carbon percentage we have determined in various specimens; it varies between 43 and 44. It is largely soluble in alkalies, the solution reducing Fehling solution copiously on boiling.

Pine-wood we find gives similar results, _i.e._, a high percentage of a product of low carbon percentage, soluble for the most part in cold alkaline solutions, and agreeing in this as in other respects with the well-characterised group of oxycelluloses.

The soluble products of the chromic acid oxidation we have isolated and find to be brown gummy bodies, giving chlorine substitution products with characteristic colour reactions.

By this particular oxidation, therefore, we appear to convert into cellulose (_i.e._, a derivative of cellulose) a body which, under the treatment hitherto adopted for separating the cellulose, is _hydrolysed_ into soluble products. We have on many occasions pointed out that the yellow chlorinated derivative obtained from the fibre contains a _quinone-chloride_ associated with a body which gives a copious yield of furfurol by acid hydrolysis, and probably, therefore, a _pentaglucose._

It is therefore probable that this pentaglucose exists in the fibre in the form of a cellulose (Comp. E. Schulze, _Berl. Ber._, xxiv., 2277).

There are many grounds for regarding lignification as a process of modification of cellulose by deoxidation and dehydration, and the action of dilute chromic acid in presence of a hydrolysing acid would appear to confirm this view, while giving the nearest approach which we have yet made to the retracing of the process backwards through its several stages.

We are engaged in following up these observations, which cannot fail to afford many new links in the chain of evidence by which the celluloses are being connected with bodies of definite constitution.

Laboratory, 4, New Court, London, W.C.
July 30, 1891.

CONTRIBUTIONS TO MICRO-CHEMICAL ANALYSIS.*

By H. BEHRENS.

(Continued from p. 53).

XIV.—_Cadmium._

1. With sodium bicarbonate. Round granules of 2—3 micro., diameter refracting light strongly (see Zinc 1). On account of the finely granular texture of the precipitate, the deposition of cadmium by sodium bicarbonate is decisive, only if performed in an ammoniacal solution from which magnesium, nickel, &c., have been previously removed by means of phosphorus salt. Limit of the reaction at 0·00001 m.grm. Cd.

2. With oxalic acid. Rhombs and parallelopipeds of the oxalate $Cd,C_2O_4+3H_2O$, belonging to the monoclinar system, twice as large as the crystals of zinc oxalate, extinguishing at 24°. If more than 30 per cent of zinc are present the form of zinc oxalate prevails exclusively. Limit of the reaction at 0·00034 m.grm. Cd.

The solution of cadmium oxalate in ammonia yields

on evaporation rods and tables, but in presence of zinc sphærolites which present nothing characteristic. Acids and salts of aluminium, chrome, and iron prevent the precipitation of cadmium oxalate. The cadmium may be conveniently thrown down from an ammoniacal solution as under 1, and after drawing off the ammoniacal liquid the granular precipitate can be converted into the crystalline oxalate by adding a granule of oxalic acid.

3. With ammonium-mercury sulphocyanide. Massive, rectangular prisms and pseudopyramids, in presence of zinc, merely the forms of zinc-mercury sulphocyanide. With cobalt blue mixed crystals. Limit of the reaction at 0·001 m.grm. Cd.

4. With potassium ferricyanide. Yellow, cubic crystals of 3—4 micro., not distinguished from those of zinc ferricyanide. Limit of the reaction at 0·00003 m.grm. Cd.

Metallic magnesium precipitates zinc and cadmium readily and completely from slightly acidulated solutions. From the grey metallic sponge the chief part of the zinc may be extracted by boiling acetic acid.

XV.—_Cerium, Lanthanum, Didymium._

1. With sodium sulphate. Heavy, white precipitate of a crystalline structure, the formation of which in dilute solutions is promoted by heat. Strong acids, especially sulphuric acid, interfere. The precipitate consists of small lenticular discs and rounded rods, varying in length from 4 (for Ce) to 10 micro. (Di). Potassium sulphate throws down discs of 4—6 micro. Thallous sulphate slowly precipitates hexangular colourless tables up to 100 micro. All these double salts are decomposed by sodium carbonate, potassium ferrocyanide, and oxalic acid. Limit of the precipitation—

For Ce at 0·00002 m.grm.
  ,, La ,, 0·00004 ,,
  ,, Di ,, 0·00007 ,,

2. With sodium carbonate. Flocculent precipitates, that of lanthanum whitish, the others in transmitted light brownish. In an excess of the reagent crystallisation ensues in time. Lanthanum carbonate is, after half an hour, completely converted into pale, oval leaflets and thistle heads of 40—70 micro. Cerous carbonate forms more slowly spiked globes and acute rhombs of 10—40 micro. Didymium carbonate requires at least an hour, and the crystallisation does not extend beyond the formation of crystalline nodules of 12—20 micro. Limit of the reaction for Ce at 0·00005 m.grm., for La 0·00006 m.grm., for Di 0·0001 m.grm.

3. With oxalic acid we obtain at first white, pulverulent precipitates, which in an excess of the precipitant quickly become fine needles. Cerium yields after a few minutes crosses of 70, and imperfect squares of 40 micro. Lanthanum yields needles and prolonged rhombs of 60 micro. grouped in sheaves. Didymium produces crosses and sphærolites like cerium. Limit of the reaction for cerium 0·00004 m.grm.; for lanthanum 0·00006 m.grm., for didymium at 0·0001 m.grm.

4. Potassium ferrocyanide produces granular precipitates. With cerium transparent, colourless grains of 4—6 micro., and partly rounded cubes. With lanthanum clear rhombs of 50 micro. An excess of the reagent modifies them into barrel-shaped prisms, and deposits colourless hexagons and hexagonal prisms of 30—60 micro. With didymium hexagons with depressed angles, rosettes radially ribbed, stars and dendrites of about 60 micro. The largest specimens are distinctly violet-grey. Limit of the reaction for cerium and lanthanum at 0·0001 m.grm., for didymium 0·00015 m.grm.

For distinguishing the cerium metals, methods of separation must be used. From the mixed oxalates, or by melting the double sulphates with soda, mixed oxides may be obtained from which dilute nitric acid chiefly extracts lanthanum and didymium, the solution may then be evaporated, and the bulk of the didymium nitrate may be decomposed by cautious fusion. For further exami-

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* _Zeit. Anal. Chemie._

nation the reactions 2 and 4 are to be preferred. 0·1 grm. of the mixed double sulphate is a sufficient quantity for separation.

XVI.—*Yttrium-Erbium.*

1. Oxalic acid precipitates neutral and faintly acid solutions in the state of extremely fine crystals. By means of a plentiful addition of hydrochloric acid crosses of 25 micro. may be obtained. The limit of the reaction is at 0·005 m.grm. Y.

2. If the oxalate is dissolved in ammonium carbonate, tetragonal pseudo-octahedra are obtained of 10—25 micro. If to a solution of yttrium-erbium carbonate in ammonium carbonate there is added a little ammonium oxalate, the finely crystalline precipitate may be converted into the ordinary crystals by repeated heating, and replacing the water and ammonium carbonate which have been expelled. The reaction in this form is very useful.

(To be continued).

CONTRIBUTIONS TO THE CHEMISTRY OF ERBIUM AND DIDYMIUM.*
(First Communication.)

By GERHARD KRUSS.

AMONGST the least readily accessible departments of inorganic chemistry must doubtless rank the chemistry of the metals of the rare earths, Most distinguished inquirers—Berzelius, Mosander, Bunsen, Marignac, Rammelsberg, Cleve, Nilson, Petterson, Brauner, and others —have carried on extensive researches on the metals of the cerium and yttrium group, and yet our knowledge of many of the rare earths is still but fragmentary. Thus, for instance, the oxides of terbium, thulium, and holmium are hitherto approximately diagnosed by few characters only, and it is even questionable if these earths are unitary bodies. Even erbium and didymium, whose oxides rank with the earths which have been most closely studied (at least among those which produce absorption spectra), are as yet by no means certainly characterised, and cannot be introduced with certainty into the natural system of the elements.

If, despite the most strenuous labours of many inquirers, the veil which still enshrouds the true nature of erbium and didymium has been raised only partially and slowly, time spent in this region of chemistry did not seem to promise, *a priori,* any rapid and abundant scientific returns. Still the author has ventured to penetrate a little further into the chemistry especially of erbium and didymium, the rather as the periodic system is but imperfectly developed in its middle series, to which erbium and didymium—or perhaps their constituents— must belong. These researches were supported most liberally by The Elizabeth Thomson Science Fund, for which the author here returns his best thanks to the Trustees of that Foundation.

In the following treatise are given the results of certain experiments made for the purpose of discovering more convenient methods for isolating the earths, as well as certain means for diagnosing the erbium and didymium hitherto so called.

At present we understand by the names erbium and didymium different bodies from those which were so called in the years 1870 to 1880. That oxide which about twenty years ago was known as erbia, and was regarded as the oxide of an individual earth, consists—according to the interesting researches of Marignac, Soret, Nilson, Cleve, Brauner — of at least seven distinct earths, scandia, ytterbia, thulia, erbia, terbia, Soret's X, and yttria. Further, a few years ago, Lecoq do Boisbaudran, by the

Liebig's Annalen.

fractionated precipitation of Soret's X and the spectroscopic examination of the several fractions, showed that X, or Cleve's holmium, consists of at least two elements. It further results, from the interesting researches of Crookes, that yttria is not the oxide of a chemical individual.

Thus "old" erbium has gradually been resolved into an extensive series of elements. A similar lot has occurred to that body which, in the last decennium, was known simply as didymium. This also has been broken up, firstly into Dβ (Brauner's Z), or samarium and true didymium ; and the latter, again, as it appears from the researches of Auer von Welsbach, consists of at least two distinct elements, neodymium and praseodymium.

Such was the condition of the chemistry of the rare earths when, some time ago, L. F. Nilson and the present writer demonstrated—by a spectroscopic examination of the rare earths obtained from the thorites, euxenites, fergusonites, wœhlerites, and cerites of different localities—that the rare earths which yield absorption spectra (erbium, holmium, thulium, didymium, samarium) consist of a far greater number of components than it might be assumed from the investigations of Soret, Lecoq de Boisbaudran, Auer von Welsbach, and others. The spectroscopic examination of the several fractions obtained by the fractionated decomposition of the nitrates of the earths of fergusonite and euxenite proved how impossible it is *completely* to resolve the entire erbia and didymia into its separate constituents by the often-employed method of a partial decomposition of the nitrates. This is especially the case if we have at our disposal only a few kilos. of initial material. (For the detailed results of this investigation the reader is referred to *Ber. Deutsch. Chem. Gesell.,* xx., 2134.)

As little did Lecoq de Boisbaudran succeed in a complete resolution of Soret's X by a combination of the fractionated decomposition (by heat) of the nitrates, and fractionated precipitation of the solutions of the nitrates with ammonia. Even Auer von Welsbach's method of a fractionated crystallisation of the double ammonium nitrates in a strongly acid nitric solution was not capable of entirely resolving didymium into its individual constituents. According to the experiments of Krüss and Nilson, neodymium and praseodymium are still compound bodies. This observation was confirmed by the researches of A. Bettendorff on the earths of the cerium and yttrium groups recently published in the *Annalen* (cclvi., p. 159).

Hence up to the present date we have not yet succeeded in completely isolating any one constituent of the rare earths which yield absorption spectra, and characterising it with certainty as an element. The very slightly differing basicity of these earths, and the solubilities of their salts, which are almost alike, impede in the highest degree the solution of this problem.

Elsewhere (*Ber. Deutsch. Chem. Gesell.,* xxi., p. 2310) the author has pointed out that we may approach nearer to our purpose if we observe that nature has deposited some or other constituents of the rare earths which yield absorption spectra, together or separate in one or other mineral, as obtained from this or that locality.

It appeared, also, from the researches on the components of the rare earths by Krüss and Nilson, quoted above, that *e. g.* of the simple constituents of the "old" earth X, which have been named Xα, Xβ, . . . Xη, the nitrate solutions of which display in their spectrum characteristic absorption bands, there occur in—

Mineral.	Only the Elements.
Thorite from Brevig	Xα, Xδ, Xη.
,, Arendal.. ..	Xβ, Xγ, Xε, Xζ, Xη.
Wœhlerite from Brevig ..	Xγ, Xζ, Xn.
Cerite from Basstnäs	Xα, Xη.
Fergusonite from Arendal ..	Xβ, Xγ, Xδ, Xε, Xζ, Xη.
,, Ytterby }	Xα, Xβ, Xγ, Xδ.
Euxenite from Hitterö and }	
Arendal .. .. .. }	Xε, Xζ, Xη

Nature has thus effected a partial separation of these elements which approximate so closely in their properties, and, in order as far as possible to utilise this fact in the further study of the rare earths, it seemed advantageous to institute a further spectroscopic revision of the basic constituents of rare minerals from the most different localities. For this purpose there were utilised the above-mentioned researches of Krüss and Nilson, and from this point of view experiments have been recently made by P. Kiesewetter and G. Krüss.

In addition to a series of thorites, euxenites, ferguson-ites, wœhlerites, cerites, keilhauites, and monazites, from different localities, the author has made the closest spectrocospic examination of a number of other minerals in search of the earths of the erbium and didymium earths, and he has undertaken by the best-known methods to isolate one or the other constituent of erbium or didymium from the minerals where it seemed most richly accumulated. It is certainly possible in this manner to obtain peculiar spectra of erbium and didymium, and abnormal spectra of holmium, in which the relative intensities of the several absorption lines are quite different from those commonly occurring. But I must admit that, whilst using the accepted methods of separation for the rare earths, I have never succeeded in obtaining perfectly unitary, homogeneous bodies, the molecular weights of which remained absolutely constant on further treatment.

When, *e. g.*, I had succeeded in obtaining a few grms. of a didymium earth which displayed in the absorption spectrum of its nitric solution almost *one* only double band in the green, and if then large quantities of the same didymia earth were prepared in the same manner, there appeared, on the spectroscopic examination of a more concentrated solution in a stratum of several decimetres in thickness, along with the extremely intense double band in the green, a series of other very faint lines of absorption.

Without doubt we are still in want of methods for the separation of the rare earths which are even approximately exact, and some of the methods hitherto applied have not been developed in a trustworthy manner. Considerable weights, therefore, of crude material were used, and in obtaining ordinary erbia and didymia a series of methods of separation, partly new and partly old, were studied. The oxides, as obtained by different methods, were always carefully examined for their homogeneity, both spectroscopically and by a determination of their molecular weights.

Preparation of Erbium and Didymium Salts from Gadolinites, avoiding the method of fractionating the rare earths by long series of decompositions, by heating their nitrates :—

In order to separate erbium from didymium, the method proposed by Mosander and developed by Bunsen has generally been applied, depending on the different solubility of the double potassium salts of both earths. This method by no means admits of an exact separation of the didymium from the yttrium earths. Even if the solution of the mixed earths is saturated for several days with potassium sulphate, until there no longer appears any precipitate of the double sulphates, several didymium lines may still be observed in the spectrum of the yttria earths, and erbium and holmium lines on the spectrum of the earths precipitated by potassium sulphate. (See Krüss and Nilson, *Ber. Deutsch. Chem. Gesell.*, xx., p. 2140). Nilson previously (*ibid.*, xv., p. 2525) pointed out the imperfection of this method of separating didymium from the yttria earths.

That there exists a very considerable difference in the respective solubilities of the double sulphates of potassium, didymium, and erbium is indubitable ; it had therefore to be tried to separate erbium from didymium by fraction-ated crystallisation with potassium sulphate. The results which Dr. K. Bröckelmann obtained in some experiments of this kind were as follows ·—

Hot concentrated acid solution of potassium sulphate was added to the faintly acid solution of the nitrates of the rare earths until a crystalline precipitate appeared. It was filtered off hot, and washed with hot concentrated solution of acid potassium sulphate until the washings no longer produced a precipitate with ammonia. The washings were mixed with the filtrate, the solution again precipitated in the same manner, and this treatment was repeated until an excess of potassium sulphate added to the filtrate of the last precipitate no longer determined a precipitate.

(To be continued.)

THE DETERMINATION OF CARBON IN STEEL.[*]

By A. A. BLAIR.

PROF. J. W. LANGLEY has given in his excellent paper (*Journal of Analytical and Applied Chemistry*, vol. iv., p. 403), read at the joint session of the American Institute of Mining Engineers, and the British Iron and Steel Institute at Pittsburgh, a clear history of the first part of the work of the American members of the International Steel Standards Committee in their investigation of the various methods for the determination of carbon in steel.

As regards the combustion method, the results as stated by Prof. Langley may be briefly summarised as follows :—Dr. Dudley showed in a most interesting series of results that the double chloride of copper and ammo-nuim contained some form of organic matter which united with the carbonaceous matter liberated from a steel by the action of this solvent, the amount of the organic matter varying with the purity of the double chloride, and diminishing with each crystallisation of the salt. The remarkable fact which I discovered, that a very acid solution of the double chloride gave higher results than a neutral solution, was quickly verified by both Prof. Langley and Dr. Dudley. Dr. Dudley thought that the acid caused a precipitation of organic matter from the double chloride, while my view was that a neutral solution is rendered slightly alkaline by the solution of the metallic iron and the precipitated copper, and that this alkaline solution dissolves some of the carbonaceous residue which is not subsequently precipitated by the addition of acid.

It was agreed, after the reading of Prof. Langley's paper, that I should continue this investigation, and the results have proved of so much interest to the American Committee that it is deemed advisable to make them public now, that the profession at large may have the benefit of the suggestions they offer without undue delay.

My combustion apparatus consists of a platinum tube 26 inches long and 9·16 of an inch in diameter, the forward part inside the furnace being filled for a distance of six inches with granulated oxide of copper held in place by two plugs of platinum gauze. A plug of platinum gauze completely filling the bore of the tube is inserted after the boat, and occupies the portion of the tube at the rear of the furnace.

The oxygen and air are contained in cylinders under pressure, and each passes through its own purifying apparatus consisting of a bulb containing caustic potassa, 1·27 specific gravity, followed by a 12-inch U-tube containing broken pieces of pumice stone. Following each U-tube is a tube fitted with a glass stop-cock leading into a T-tube which connects directly with the end of the combustion tube. By this arrangement the oxygen and air are under perfect control, and there is no danger, as in the ordinary manner of drawing the air through the apparatus by means of an aspirator, of introducing into it any gases that may be in the laboratory. The purifying train for the products of combustion consists of a U-tube contain-

ing in the limb nearest the combustion tube anhydrous sulphate of copper in pumice, and in the other, turnings of metallic copper, followed by another U-tube containing chloride of calcium. In the absorption apparatus the ends of the Liebig bulb and one end of the tube are fitted when on the balance with short pieces of very fine capillary glass tubing; the other end of the tube is fitted with a cap of rubber tubing, the outer end of which is squeezed together and cemented. This arrangement allows the passage of sufficient air to equalise the pressure in the absorption apparatus, but the capillary openings are too small to permit the loss or gain of moisture during the operation of weighing.

In all cases I used the "factor" weight of the drillings (2·7273 grms.), so that each 0·0001 grm. of carbonic acid obtained in the absorption apparatus is equal to 0·001 per cent of carbon in the steel.

I determined in the first place to repeat Dr. Dudley's experiments on the re-crystallisation of the double chloride of copper and ammonium, and therefore prepared a solution by mixing commercial chloride of copper and chloride of ammonium, adding ammonia until a slight precipitate formed, allowing this to settle, syphoning off the clear solution and filtering it through ignited asbestos. This I called solution "A."

Using 200 c.c. of solution "A" and 20 c.c. hydrochloric acid, I obtained :—

No. 1, carbon .. .. .. 1·046 per cent.
„ 2, „ .. .. .. 1·047 „
„ 3, „ .. .. .. 1·044 „
„ 4, „ .. .. .. 1·049 „

Using 200 c.c. solution "A" without the addition of hydrochloric acid, keeping the solution as neutral as possible, and washing with acidulated solution "A" to get rid of the basic salts, I obtained :—

No. 5, carbon .. .. .. 1·013 per cent.
„ 6, „ .. .. .. 1·004 „

I then evaporated solution "A," and crystallised the double chloride. I washed each crop of crystals with cold water, and finally reserved the mother-liquor, which I filtered through ignited asbestos, calling it solution "B." The crystals dissolved in water and filtered through asbestos I called solution "C." Using 200 c.c. of solution and 20 c.c. hydrochloric acid I obtained :—

Solution "B."

No. 7, carbon .. .. .. 1·076 per cent.
„ 8, „ .. .. .. 1·067 „

Solution "C."

No. 9, carbon .. .. .. 1·027 per cent.
„ 10, „ .. .. .. 1·029 „

I then crystallised about a gallon of the solution which I have in constant use, which is made by dissolving the salt that I buy as "c. p. crystallised double chloride of copper and ammonium," in water, adding slight excess of ammonia, allowing to stand for several days, syphoning off, and filtering the clear liquid through ignited asbestos. The mother-liquor that I obtained I called solution "D," and the solution of the re-crystallised salt solution "E," with which I made two determinations, adding 15 c.c. hydrochloric acid to one, and leaving the other neutral with the following results :—

Solution "D."

No. 11, (acid) carbon . .. .. 1·064 per cent.
„ 12, neutral carbon .. .. 1·022 „

Solution "E."

No. 13, (acid) carbon . .. .. 1·028 per cent.
„ 14, (neutral) carbon .. .. 0·998 „

I then prepared a solution of chloride of copper by igniting 250 grms. of pure oxide of copper in platinum at a red heat for thirty minutes, dissolving in hydrochloric acid, evaporating to dryness, re-dissolving in water, and filtering through asbestos. The solution which contained 28 grms. of cupric chloride to 100 c.c. I called solution "F." With this I made four determinations, two with 20 c.c. of hydrochloric acid added to the solution, and two with the solution kept as neutral as possible.

Solution "F."

No. 15, (acid) carbon . .. .. 1·034 per cent.
„ 16, „ „ . .. .. 1·034 „
„ 17, (neutral) carbon .. .. 1·034 „
„ 18, „ „ .. .. 1·033 „

It required two days to effect solution in the acid determination, and three days in the alkaline, with constant stirring.

I then made four determinations, using 125 c.c. of solution "F," 15 c.c. hydrochloric acid, and 1, 2, 3, and 4 times the molecular equivalent of chloride of ammonium. The latter I made by neutralising C. P. hydrochloric acid with C. P. ammonia. The results are as follows :—

P. c.
No. 19, (1 equiv. of chloride of ammonium) carbon 1·038
„ 20, (2 „ „ „ „ 1·055
„ 21, (3 „ „ „ „ 1·055
„ 22, (4 „ „ „ „ 1·073

I then fused chloride of potassium, and added it to 125 c.c. portions of solution "F" with 15 c.c. hydrochloric acid, with the following results :—

P. c.
No. 23, (1 equiv. of chloride of potassium) carbon 1·036
„ 24, (2 „ „ „ „ 1·036

Solution of the drillings with the potassium salt is as rapid as with the ammonium salt, occupying about twenty minutes with the "special carbon standard."

I now determined to try the direct combustion of the steel in oxygen, and for this purpose I had a platinum boat made six inches long, and just large enough to go in my combustion tube. I had a cover of platinum foil made for the boat with a half circle cut through about every half inch. On raising these semi-circular pieces to an angle of about 45°, they made a series of little wings which directed the current of gas flowing along the top of the tube down into the boat. I selected for this purpose the finer portion of the drillings, and after the combustion I withdrew the boat, ground the magnetic oxide in an agate mortar to expose any metallic particles that might remain unacted upon, and burned it a second time. In no case did I get the slightest increase in the weight of my absorption apparatus by the second combustion.

No. 25, carbon .. .. .. 1·031 per cent.
„ 26, „ .. .. .. 1·020 „
„ 27, „ .. .. .. 1·024 „
„ 28, „ .. .. .. 1·032 „

Finally I made a determination of carbon by volatilising the iron in a current of dried hydrochloric acid gas which had been passed through a porcelain tube filled with charcoal and heated to bright redness. This gave me :—

No. 29, carbon .. .. .. 1·024 per cent.

I then procured from a firm of manufacturing chemists a lot of crystallised double chloride of copper and potassium, and made a solution by dissolving 300 grms. of the salt in a litre of water and filtering through ignited asbestos. Using 200 c.c. of this solution and 15 c.c. strong hydrochloric acid, I obtained :—

No. 30, carbon .. .. .. 1·035 per cent.
„ 31, „ .. .. .. 1·038 „

Dr. Dudley's theory of the double chloride of coppe

and ammonium containing organic matter, which is liberated in the treatment of steel, attaching itself to the carbonaceous residue, and thus increasing the apparent carbon contents of the steel, seems proved by his own determination as well as by the results Nos. 7, 8, 11, 19, 20, 21, and 22; the last four results led me to believe, however, that this organic matter comes from the chloride of ammonium, and is a hydrocarbon derived from the gas liquor from which all ammonia salts are now made.

My own theory, that the copper solution must be strongly acidified to give correct results, received strong support from the determinations Nos. 5, 6, 12, and 14; for these, as well as my previous determinations, point strongly to a solution of the carbonaceous matter by the alkaline salts in the absence of an excess of acid. The striking results obtained from the chloride of copper solution " F " show plainly that an excess of acid does not cause a loss of carbon, while it very much facilitates the solution of the steel. I then obtained from Prof. Langley some very fine drillings of the same steel, and using the six-inch boat described above I obtained :—

No. 32, carbon .. .. .. 1·032 per cent.
  „ 33,   „   .. .. .. 1·030   „
  „ 34,   „   .. .. .. 1·031   „

To test the effect of using a purifying apparatus that had been used for combustions of the carbonaceous residue liberated by the double chloride, I made several combustions of these residues and, without changing the apparatus, a direct combustion. The result was :—

No. 35, carbon .. .. .. 1·042 per cent.

This last result, taken in connection with many others that I had previously obtained, suggested to me the desirability of using some substance in my purifying apparatus that would not only prove more efficient, but would render unnecessary the constant changes and delays involved by a number of sets of purifying tubes and the necessity for changing the anhydrous cupric sulphate in pumice. It has been my practice to use one set of purifying tubes for three combustions only, then to substitute another set, and while this was in use to purify the first set by placing the limb of the U-tube that contained the cupric sulphate in a copper box, heat the box to about 200° C., and draw air, previously dried by passing it through a jar of chloride of calcium, through the apparatus. I therefore instituted a series of experiments on this subject, being finally led to try cuprous chloride on the theory that small amounts of hydrochloric acid gas and chlorine, when brought in contact with cuprous chloride, would be absorbed, the chlorine oxidising the cuprous to cupric chloride. I then prepared a purifying train consisting of two Marchand U-tubes, the first of which contains in the bulb *a* granulated dried cuprous chloride, made by moistening the ordinary powdered salt and stirring it while drying in a capsule, until it forms into little lumps about the size of a split pea. After heating it until all the moisture is expelled it is transferred, while still hot, to the U-tube, completely filling the bulb *a*. The rest of the U-tube is filled with anhydrous cupric sulphate made by heating small crystals of the ordinary salt until the water is expelled and the salt is white. At *b* is placed a plug of asbestos to prevent small particles of cupric sulphate from being carried forward with the current of gas. The second U-tube is filled with *dried*, not fused, chloride of calcium, as the latter is apt to contain caustic lime. Cupric sulphate absorbs its own volume of hydrochloric acid gas, giving it up only when heated. With the tubes thus filled I made four combustions on the " special carbon standard ingot," using the double chloride of copper and potassium, and washing No. 36, 37, and 38 with hot hydrochloric acid and water, and No. 39 in the usual way, using cold water and acidulated double chloride. Mr. Shimer thought that by washing with hydrochloric acid and hot water there

was less hydrochloric acid left in the carbonaceous residue, and I wanted to see whether there was any possibility of getting lower results in this way due to the action of the acid and hot water on the carbonaceous residue.

No. 36, carbon .. .. .. 1·030 per cent.
  „ 37,   „   .. .. .. 1·029   „
  „ 38,   „   .. .. .. 1·033   „
  „ 39,   „   .. .. .. 1·026   „

The results were all low, and I should have been inclined to refer it to the method of washing, but that No. 39, washed in the usual way, was the lowest of all. It then occurred to me that anhydrous cupric sulphate being much more hygroscopic than chloride of calcium, the oxygen and air left the absorption apparatus with more moisture than they had when they entered it after passing through the purifying train. If this were true then the
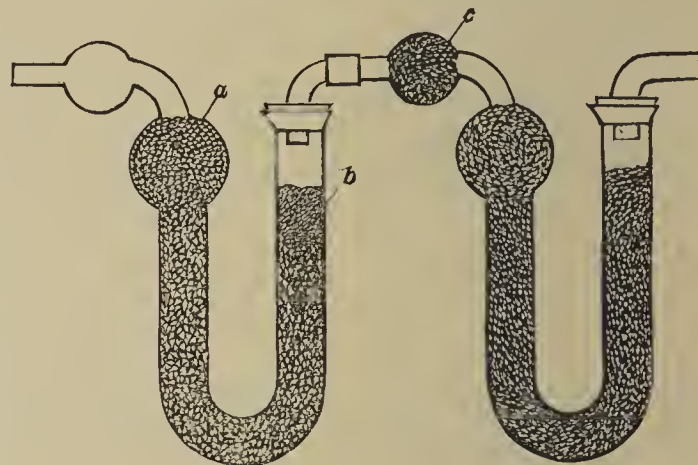
greater the volume of oxygen and air passed through the apparatus, the lower the result. To prove this I made a direct combustion on the fine sample, the time occupied being about ninety minutes instead of the usual thirty-five minutes necessary to burn the carbonaceous residue. The combustion followed immediately after No. 39, the result being :—

No. 40, carbon .. .. .. 1·006 per cent.

This seemed quite conclusive as to the cause of the low results, and to overcome the difficulty I introduced a small plug of cotton into the bulb *c* of the chloride of calcium tube, and moistened it with one or at most two drops of water. Another direct combustion on the fine sample gave :—

No. 41, carbon .. .. .. 1·037 per cent.

I then made a number of combustions in the course of my ordinary work, removing the plug of cotton in *c* after each day's work, and putting in a fresh one duly moistened before each new set of combustions. After the lapse of several days I made two more determinations on the " special carbon standard ingot," No. 42 on the carbonaceous residue and No. 43 a direct combustion. They were respectively the fourth and fifth combustions of a series made at one time, and No. 43 was the twenty-third combustion made without heating the purifying apparatus.

No. 42, carbon .. .. .. 1·038 per cent.
  „ 43,   „   .. .. .. 1·037   „

I am led to conclude that chloride of copper and potassium is a much more safe and desirable solvent to use than chloride of copper and ammonium, and unless subsequent experience shall show some flaw in my work, cuprous chloride and anhydrous cupric sulphate are much more convenient and much safer reagents for purifying the gas than any substances previously used.

This series of experiments illustrates in a striking way the value of a "standard" in work of this character. The carbon once established in a sample, each experiment has an increased value, for the result is known to be not only a departure from the mean of many analyses, but a variation from the absolute amount. The value of a method or the deficiency of an arrangement of apparatus is thus made evident at once, and the error is much more readily referred to its real source than would otherwise be possible.

Analytical chemists all over the world will owe Prof. Langley a debt of gratitude, not only for his suggestion that led to the establishment of the International Committee, but for his subsequent work which has made it possible to carry out his original idea.

THE BIOLOGICAL FUNCTION OF THE LECITHINES.
(PRELIMINARY NOTICE).
By W. MAXWELL.

IN an earlier stage of the study of the lecithines I showed, in an article entitled "On the Behaviour of the Fatty Bodies, and the Rôle of the Lecithines During Normal Germination" (*American Chemical Journal*, xiii., No. 1), that the inorganic phosphorus present in the mature seed, under the action of the processes occurring during incipient growth, becomes re-organised, and appears in the young plantlet in the organic form as a constituent of lecithine.

In the course of continuation of the researches, which have been extended or carried over from the vegetable to the animal organism, I have established the observation that the phosphorus which is present in the organic form as a lecithine in the egg of a hen, under the action of the process of incubation, becomes re-organised, and is found in the form of a mineral phosphate in the bone of the chicken.

In the light of the data to be given in a later contribution, of which this is a preliminary notice, it will be possible to indicate the course of the circulation of the element phosphorus in the three divisions of matter, and to show that it is (at least in great part) in the organic form of the lecithine, or lecithines, that the inorganic phosphorus of the mineral kingdom passes through the vegetable kingdom into the inorganic form, constituting the bone, of the animal kingdom.—*American Chemical Journal*, xiii., No. 6.

ON THE ACTION OF 66° SULPHURIC ACID ON HYDROCHINON, AND THE VALUE OF THE RESULTING SULPHO-ACID
AS A DEVELOPER FOR GELATINO-BROMIDE PLATES.
(PRELIMINARY NOTICE.)
By JAMES H. STEBBINS, JUN.

SINCE the introduction of the dry plate in photography many substances have been proposed as developers, but the only practical survivors of the substances thus proposed are pyrogallic acid, ferrous oxalate, hydrochinon, and more recently eikonogen, or the sodium salt of amido-β-naphtholmonosulpho acid. Having at one time had occasion to employ hydrochinon as a developer, I was struck with the beautiful qualities of the plates developed by its means, but, although hydrochinon is *per se* a most excellent developer, it has, nevertheless, several drawbacks, among which are its limited solubility in water, and it was this very question of solubility which started me upon the present investigation. It seemed that if hydrochinon could be converted into a mono-sulpho acid, that its solubility would be very materially increased, and if this could be accomplished without in any way affecting its reducing qualities for the haloid salts of silver a very material improvement would be obtained.

Finding only very meagre information in the literature upon this subject, the following experiments were made :—

Experiment 1.

Twenty grms. of 66° sulphuric acid were mixed with 10 grms. of hydrochinon, and then heated under constant stirring upon the steam bath, until the hydrochinon was all dissolved. The stirring was kept up for a few minutes longer, when suddenly the whole contents of the beaker solidified to a cake of small straw-coloured needles.

The cake was broken up and dissolved in cold water, in which it is very soluble ; then converted into its lime salt by neutralising the acid solution with calcium carbonate. The precipitate of calcium sulphate was filtered off, and the filtrate of the lime salt placed upon the steam bath for concentration. After a short exposure to the air the solution began to darken, showing that oxidation was taking place. Concentration by this means had therefore to be abandoned. The solution was then placed under the air-pump over sulphuric acid, hoping that by this means it may be concentrated without spoiling, but even in this case oxidation kept slowly taking place. It was therefore decided to treat the mixture with an excess of sodium sulphite, and then concentrate *in vacuo* over sulphuric acid. On adding the sodium sulphite, calcium sulphate was precipitated, carrying considerable of the colouring-matter with it. The precipitate was filtered off, and the filtrate containing the sulpho-acid of hydrochinon was placed under the bell jar of the air-pump over sulphuric acid, to concentrate, but owing to an accident the contents of the beaker were spilled, and therefore the experiment had to be repeated.

Experiment 2.

Ten grms. of hydrochinon were treated as before, with 20 grms. 66° sulphuric acid. After the reaction the mixture was dissolved in water, heated upon the water-bath, and neutralised with barium carbonate.

The barium sulphate was filtered off, and the filtrate containing the barium salt of the sulpho-acid was concentrated *in vacuo* over sulphuric acid. The barium salt thus obtained crystallised much more readily than the calcium salt, and the solution of the same in water does not appear to be as readily oxidisable as the former when exposed to the air. It crystallises from its aqueous solution in white, warty, concretions of star-grouped crystals (needles).

A sample of the above barium salt, obtained by rapidly boiling down a portion of its aqueous solution to dryness and then further drying over sulphuric acid, gave the following results :—

Water of Crystallisation.

0·2810 grm. substance lost 0·0081 grm. H_2O.
Equivalent to water 2·88 per cent., or 1 mol. water of crystallisation.

Ba *Estimation*.

0·2810 grm. sub. gave 0·116 grm. $BaSO_4$.

Equivalent to Ba .. .. 24·26 p. c.
Equivalent to Ba in anhydrous salt .. 24·98 ,,

On now attempting to calculate the molecular weight of the barium salt from the amount of barium sulphate formed, we get the following :—

0·2729 anhydrous salt gave 0·116 grm. $BaSO_4$.
0·116 : 233 ($BaSO_4$) :: 0·2729 : x ; $x = 548·1$.

The least molecular weight of the salt, carrying one atom of barium, is therefore 548·1.

One atom of barium might belong, however, to a substance containing either one or two sulpho-groups : but the theoretical molecular weight of barium hydrochinon disulphonate is 406, whereas the theory for barium hydrochinon monosulphonate is 515 (calculated from the formulæ $\left(p. C_6H_3 <^{OH}_{OH} {-}SO_3 \right)_2 Ba$), and consequently the former is excluded. Therefore the substance analysed is beyond much doubt the barium salt of a hydrochinon mono-sulpho-acid.

On calculating the molecular weight from the salt containing water of crystallisation we get—

$$0.116 : 233 :: 0.281 : x; \quad x = 564.$$

The theoretical molecular weight of the hydrated salt, or rather salt containing water of crystallisation, is 533.

The theoretical amount of barium called for in the anhydrous salt is 26.6 per cent.

The theoretical amount of barium in the hydrated salt is 25.7 per cent.

The amount of water of crystallisation found is 2.88 per cent ; therefore—

$$2.88 \div 18 :: 0.16 \text{ mol. } H_2O.$$

That is to say, that 100 parts of barium salt contain 0.16 mol. H_2O of crystallisation ; therefore 548 parts of barium salt will contain—

$$100 : 0.16 = 548 : 4; \quad 4 = 0.87 \text{ mol. } H_2O,$$

or, in round numbers, 1 mol. H_2O. We have therefore found—

Barium .. .. 24.26 per cent.
Water of crystallisation .. 2.88 　　　,,
Molecular weight .. .. 564.

Whereas theory calls for—

Barium .. .. 25.7 per cent.
Water .. .. 3.40 　　　,,
Molecular weight .. .. 533.

The formula of the barium salt is therefore, without much doubt,—

$$p. C_6H_3 <^{OH}_{OH} {-}SO_3 \\ p. C_6H_3 <^{OH}_{OH} {-}SO_3 \Big> Ba + H_2O.$$
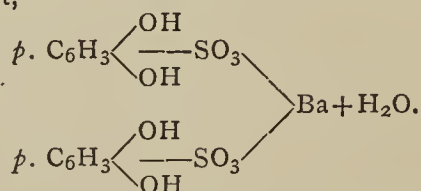
The barium salt is readily soluble in cold water and dilute alcohol, and insoluble in strong alcohol. It crystallises from dilute alcohol in white six-sided prisms. On adding ferric chloride to its aqueous solution, a momentary deep blue colouration is obtained, which, almost immediately, changes into a dirty yellow colour.

Potassium Salt.

This salt was obtained from the barium salt, by decomposing the latter with the theoretical amount of potassium carbonate. On rapidly concentrating the aqueous solution of the same, out of contact with the air as much as possible, it is obtained in the shape of little yellowish-white needles. Better results, however, are obtained by adding three or four volumes of alcohol to the concentrated aqueous solution, and then allowing the mixture to evaporate under the bell jar of an air-pump. It is readily soluble in water.

Free Acid.

$$p. C_6H_3 - \left(HSO_3 \right) \begin{cases} OH \\ OH. \end{cases}$$

The free acid may be obtained from the barium salt by accurately decomposng the latter with dilute sulphuric acid, filtering off the $BaSO_4$, shaking up the filtrate with ether, and then distilling off the latter and allowing to crystallise. A simpler method, and one that works very well, is to place the cake resulting from the action of H_2SO_4 upon the hydrochinon, upon porous tiles, till the greater part of the excess of sulphuric acid has been absorbed. Then press the mass between filter-paper until nearly every trace of H_2SO_4 has been removed. The mass thus obtained is dissolved in as little alcohol as possible, and set aside to crystallise under the air-pump. The free acid is thus obtained in long, well-defined, brownish, transparent, rhombic prisms (some of the crystals were over 1 c.m. long), containing alcohol of crystallisation. When exposed over sulphuric acid it effloresces, giving off a part, or all, of its alcohol of crystallisation.

0.1155 grm. substance over H_2SO_4 lost 0.0087 grm. alcohol, = 7.53 per cent. On now heating to 120° C. the said free acid lost 0.004 grm. more of alcohol. It will therefore be seen that the larger part of the alcohol of crystallisation is lost over H_2SO_4.

The total amount of alcohol lost is therefore 0.0087 + 0.004 = 0.0127 grm. = 10.9 per cent.

This equals 0.43 molecule, or, in round numbers, one-half molecule alcohol of crystallisation.

Theory for $C_6H_3(HSO_3)(OH)_2$. One-half C_2H_6O calls for alcohol 10.7 per cent.

It begins to fuse at 98° C., and is completely fused at 104° C. (uncorrected). Dissolves readily in water and alcohol.

Reducing Action upon the Haloid Salts of Silver.

It was thought that the best way to test this question would be to submit some exposed gelatin dry plates to the action of the hydrochinon monosulpho-acid. For this purpose a preliminary test was made, using an Eatman lantern slide-plate, and a solution of the barium salt of the hydrochinon sulpho-acid, made slightly alkaline with sodium carbonate. A positive of very fair quality was thus obtained, the tone of colour being reddish brown, It developed up very slowly, however, but it is expected that better results will be obtained when using a developer of definite composition.

In conclusion I would state that I hope soon to complete experiments upon this subject, and will then submit such further results as I may have obtained.—*Journal of the American Chemical Society*, xiii., p. 155.

PROCEEDINGS OF SOCIETIES.

ROYAL INSTITUTION OF GREAT BRITAIN.
Weekly Evening Meeting, Friday, June 12th, 1891.

Sir Frederick Bramwell, Bart., D.C.L., F.R.S., Hon. Secretary and Vice-President, in the Chair.

"*The Rate of Explosions in Gases.*" By Harold B. Dixon, M.A., F.R.S., Professor of Chemistry in the Owens College, Manchester.

The rapid act of chemical change which follows the kindling of an explosive mixture of gases has of late years attracted the interest both of practical engineers and of theoretical chemists. To utilise for motive power the expansive force of ignited gases ; to minimise the chance of disastrous conflagrations of fire-damp in coal-mines ; to follow the progress of chemical changes under the simplest conditions, are some among the problems presented to us in industry or science, demanding for their solution a knowledge of the phenomena of the explosions of gases.

To understand the nature of explosions in gases it is necessary to know certain fundamental properties of the explosive mixture. With this object in view experimenters have sought to determine for various mixtures of gases,— the heat of chemical combination, the temperature of inflammation, the pressure developed, and, lastly, the rate

at which the explosion is propagated under different conditions.

It is on the last of these problems—the determination of the velocity with which the flame travels through the gas—that I have been asked to speak.

Twenty-four years ago Bunsen described a method of measuring the rapidity of the flame in gas explosions. Passing a mixture of explosive gases through an orifice at the end of a tube, and igniting the gases as they issued into the air, he determined the rate at which the gases must be driven through the tube to prevent the flame passing back through the opening and exploding inside the tube. By this method he found that the rate of propagation of the ignition of hydrogen and oxygen was 34 metres per second, while the rate of ignition of carbonic oxide and oxygen was less than 1 metre per second. Bunsen applied these results to the rate of explosion of gases in closed vessels, and his results were accepted without cavil for fourteen years.

By 1880 facts began to accumulate which seemed inconsistent with Bunsen's conclusions. For instance, between 1876-80 I had several times observed that the flame of carbonic oxide and oxygen travelled in a long eudiometer too quickly to be followed by the eye. Mr. A. V. Harcourt, in his investigation of an explosion which happened in a large gas main near the Tottenham Court Road in 1880, was led to the conclusion that the flame travelled at a rate exceeding 100 yards per second. In the winter of 1880-1 I noticed the rapid increase of velocity as a flame of carbon bisulphide with nitric oxide travelled down a long glass vessel; and shortly afterwards I attempted to measure the rate of explosion of carbonic oxide and oxygen by photographing on a moving plate the flash at the beginning and end of a long tube. The two flashes appeared to be simultaneous to the eye, but no record of the rate was obtained, for the apparatus was broken to pieces by the violence of the explosion.

In July, 1881, two papers appeared in the *Comptes Rendus*, one by M. Berthelot, the other by MM. Mallard and Le Chatelier. Both papers announced the discovery of the enormous velocity of explosion of gaseous mixtures. Other papers quickly followed by the same authors. M. Berthelot made the important discovery that the rate of explosion rapidly increases from its point of origin until it reaches a maximum which remains constant, however long the column of gases may be. This maximum M. Berthelot states to be independent of the pressure of the gases, of the material of the tube, and of its diameter above a small limit. The rate of explosion thus forms a new physico-chemical constant, having important theoretical and practical bearings. The name " L'Onde Explosive " is given by Berthelot to the flame when propagated through an explosive mixture of gases at the maximum velocity.

While Berthelot, associated with Vieille, was measuring the rate of the " explosion-wave " for various mixtures of gases, Mallard and Le Chatelier continued the study of the preliminary phenomena of explosion which precede the formation of the " wave." They showed, by photographing on a revolving cylinder,—(1) that when a mixture such as nitric oxide and carbon bisulphide is ignited at the open end of a tube, the flame travels a certain distance (depending on the diameter and length of the tube) at a uniform velocity; (2) that at a certain point in the tube vibrations are set up which alter the character of the flame, and that these vibrations become more intense, the flame swinging backwards and forwards, with oscillations of increasing amplitude; and (3) that the flame either goes out altogether, or that the rest of the gas detonates with extreme velocity. Again, when a mixture of gases was fired near the closed end of the tube, they found the velocity of the flame regularly increased, as far as their instruments were able to record the rapidly increasing pace.

Mixtures of coal-gas with air, and of fire-damp with air, show phenomena of the first and second kind.

Ignited at the open end of a tube, these mixtures burn at a uniform rate for a certain distance, and then the flame begins to vibrate.

The vibrations acquire greater or less velocity according to the nature of the mixture and the conditions of the experiment; but the third *régime* of uniform maximum velocity is not set up. In narrow tubes the explosion soon dies out.

The phenomena studied by Mallard and Le Chatelier have been observed on a large scale in explosions in coal mines. It has been noticed that little damage was caused at the source of an explosion, and for a distance varying from 50 to 80 yards from the origin of the flame, while beyond that distance fall of roof, broken tubs, and blown-out stoppings have testified to the violence exerted by the explosion. Great as the destruction is which an explosion of fire-damp and air causes in a mine, it is fortunate that these mixtures do not *detonate*.

Passing on to Berthelot's researches on the *régime* of detonation, I will briefly summarise the results he has arrived at.

The actual velocities of explosion are compared by Berthelot with the mean velocity of translation of the gaseous products of combustion, supposing these products to contain all the heat that is developed in the reaction.

For instance, we know the total heat given out when hydrogen and oxygen combine. If this heat is contained in the steam produced, we can calculate what its temperature must be if we know its heat capacity. And if we know the temperature of the steam, we can calculate the mean velocity with which the molecules must be moving. Now Berthelot supposes that the heat is all contained in the steam produced. He assumes that the heat capacity of steam is the same as the sum of those of its constituents; and he supposes, moreover, that the steam is heated at constant pressure. Making these assumptions, he calculates out the theoretical mean velocity of the products of combustion of various mixtures, and finds a close accordance between these numbers and the explosion rates of the same mixtures. He concludes that the explosive wave is propagated by the impact of the products of combustion of one layer upon the unburnt gases in the next layer, and so on to the end of the tube at the rate of movement of the products of combustion themselves. If his theory is true, it accounts not only for the extreme rapidity of explosion of gaseous mixtures, and gives us the means of calculating the maximum velocity obtainable with any mixture of gases, but it also affords us information on the specific heats of

TABLE I.

BERTHELOT'S EXPERIMENTS.

Gaseous mixture.	Velocity in Metres per Second.	
	Theoretical	Found.
$H_2 + O$ Hydrogen and oxygen.	2830	2810
$H_2 + N_2O$ Hydrogen and nitrous oxide.	2250	2284
$CO + O$ Carbonic oxide and oxygen.	1940	1090
$CO + N_2O$ Carbonic oxide and nitrous oxide.	1897	1106
$CH_4 + O_4$ Marsh gas and oxygen.	2427	2287
$C_2H_4 + O_6$ Ethylene and oxygen.	2517	2210
$C_2N_2 + O_4$ Cyanogen and oxygen.	2490	2195
$C_2H_2 + O_5$ Acetylene and oxygen.	2660	2482
$CO + H_2 + O_2$ Carbonic oxide, hydrogen, & oxygen.	2236	2008

gases at very high temperatures, and it explains the phenomena of detonation, whether of gases or of solid or liquid explosives.

Table I. shows the explosion rates found by Berthelot, compared with the theoretical velocity of the products of combustion.

Two points in Table I. favoured the view that Berthelot might have here given the true theory of explosions : first, the close coincidence between the rates of explosion of hydrogen, both with oxygen and nitrous oxide, with the calculated mean velocities of the products of combustion; and secondly, the great discordance between the found and calculated rates for carbonic oxide with both oxygen and nitrous oxide. I had previously discovered that pure carbonic oxide cannot be exploded either with pure oxygen or pure nitrous oxide. The discordance found by Berthelot was what I should have expected from my own experiments.

A consideration of Berthelot's results, published in full in the *Annales de Chemie*, led me to think it would be useful to repeat and extend these experiments. My objects were chiefly—(1) to determine as accurately as possible the rate of the explosion-wave for some well-known mixtures ; (2) to measure the rate of the explosion-wave in carbonic oxide with different quantities of steam ; and (3) to determine the influence of inert gases on the propagation of the wave.

1. The results obtained with hydrogen and oxygen, with hydrogen and nitrous oxide, and with marsh gas and oxygen, in exact proportions for complete combustion, were in close accordance with the mean results of Berthelot ; for ethylene, acetylene, and cyanogen my numbers differed appreciably, but in no case differed by more than 7 per cent from the rates observed by Be thelot :—

TABLE II.

VELOCITY OF EXPLOSION IN METRES PER SECOND.

	Berthelot.	Dixon.
Hydrogen and oxygen, H_2+O	2810	2821
Hydrogen and nitrous oxide, H_2+N_2O	2284	2305
Marsh gas and oxygen. CH_4+O_4 ..	2287	2322
Ethylene and oxygen, $C_2H_4+O_6$ ..	2210	2364
Acetylene and oxygen, $C_2H_2+O_5$ ..	2482	2391
Cyanogen and oxygen, $C_2N_2+O_4$ ..	2195	2321

The general agreement between these measurements left no room for doubt about the substantial accuracy of Berthelot's experiments. The formula he gives does therefore express, with a close degree of approximation, the rates of explosion of many gaseous mixtures.

2. The formula fails for the explosion of carbonic oxide with oxygen or nitrous oxide. This was to be expected if—in the detonation of carbonic oxide in a long tube— the oxidation is effected indirectly by means of steam, as it is in the ordinary combustion of the gas. Measurements of the rate of explosion of carbonic oxide and oxygen in a long tube showed that the rate increased as steam was added to the dry mixture, until a maximum velocity was attained when between 5 and 6 per cent of steam was present.

3. When electrolytic gas was mixed with an excess of either hydrogen or oxygen the rate of explosion was found to be altered ; the addition of hydrogen increasing the velocity, the addition of oxygen diminishing it. The addition of an inert gas, nitrogen, incapable of taking part in the chemical change, produced the same effect as the addition of oxygen,—one of the reacting substances. —only the retarding effect of nitrogen was less marked than that of an equal volume of oxygen. The retardation of the explosion-wave caused by the addition of an inert gas to electrolytic gas evidently therefore depends upon the volume and the density of the gas added. In the following table the retarding effect of oxygen and nitrogen, on the explosion of electrolytic gas, is compared :—

TABLE III.

RATE OF EXPLOSION OF ELECTROLYTIC GAS WITH EXCESS OF OXYGEN AND NITROGEN.

Volume of oxygen added to H_2+O	O_1	O_3	O_5	O_7
Rate..	2328	1927	1690	1281
Volume of nitrogen added to H_2+O	N_1	N_3	N_5	N_7
Rate..	2426	2055	1822	—

I think it a fair inference from these facts to conclude, when the addition of a gas to an explosive mixture retards the rate of explosion by an amount proportional to its volume and density, that such added gas is inert as far as the propagation of the wave is concerned, and that any change which it may undergo takes place after the wavefront has passed by — in other words, is a *secondary* change.

This principle has been applied to determine whether, in the combustion of gaseous carbon, the oxidation to carbonic acid is effected in one or two stages — an important question, on which there is little experimental evidence. If, for instance, in the combustion of a hydrocarbon, or of cyanogen, the carbon is first burnt to carbonic oxide, which subsequently is burnt to carbonic acid, the rate of the explosion-wave should correspond with the carbonic oxide reaction, in this case the primary reaction ; whereas, if the carbon of these gases burns to carbonic acid directly, in one stage, then the rate of the explosion-wave should correspond with the complete reaction.

Now, if we adopt Berthelot's formula as a working hypothesis, we can calculate the theoretical rates of explosion of marsh gas, ethylene, or cyanogen :—(1) on the supposition that the carbon burns directly to CO_2, and (2) on the supposition that the carbon burns first to CO, and the further oxidation is a subsequent or secondary reaction. On the first supposition, if 100 represents the rate of explosion of these three gases burning to carbonic oxide, the addition of the oxygen required to burn the gases to carbonic acid should *increase* the rate of explosion :—

	Marsh Gas.	Ethylene.	Cyanogen.
Calculated rate of explosion when burnt to CO_2	104	103	107

Whereas if these gases really burn first to carbonic oxide, and the extra oxygen is inert in propagating the explosion-wave, then the addition of this inert oxygen would diminish the rate of explosion :—

	Marsh Gas.	Ethylene.	Cyanogen.
Calculated rate of explosion when burnt to CO with inert oxygen present ..	92	88	87

The experiments show that if 100 be taken as the rate of explosion when the oxygen is only sufficient to burn the carbon to carbonic oxide, the following are the rates found when oxygen is added sufficient to burn the carbon to carbonic acid.

	Marsh Gas.	Ethylene.	Cyanogen
Rates found	94	92	84

The results are therefore in favour of the view that, in the explosion of these gases, the carbon is first burnt to carbonic oxide.

But stronger evidence on this point is obtained by comparing the explosion rate of these gases (1) when fired with oxygen sufficient to burn the carbon in them to carbonic acid, and (2) when nitrogen is substituted for the oxygen in excess of that required to burn the carbon to carbonic oxide. We have seen that oxygen added to electrolytic gas hinders the explosion more than nitrogen. In precisely the same way oxygen added to a mixture of equal volumes of cyanogen and oxygen hinders the ex-

plosion more than the same volume of nitrogen. The conclusion we must come to is that the oxygen added to the mixture expressed by the formula $C_2N_2+O_2$ is as inert (so far as the propagation of the explosion-wave is concerned) as oxygen added to the mixture expressed by the formula H_2+O. The same phenomena occur in the explosion of marsh gas, ethylene, and acetylene. In all these cases the substitution of nitrogen for the oxygen required to burn the carbon from carbonic oxide to carbonic acid *increases* the velocity of the explosion. These facts seem only consistent with the view that the carbon burns directly to carbonic oxide, and the formation of carbonic acid is an after-occurrence.

Finally, the rates of explosion of cyanogen and the hydrocarbons, when their carbon is burnt to carbonic oxide, have been found greater than the velocities calculated from Berthelot's formula. This accords with the observation previously made that the rate of explosion of electrolytic gas with excess either of hydrogen or oxygen is far higher than the calculated rate. It would seem probable that the theoretical rates as calculated by Berthelot should be modified, in spite of the close agreement which his numbers show. I think the low rates found, when hydrogen, marsh gas, cyanogen, &c., are exploded with equivalent proportions of oxygen, depend partly on the carbon burning to carbonic oxide, and partly on the dissociation of the steam at the high temperature. If the formula is modified in these respects, velocities can be calculated which agree with the experimental results where dissociation does not occur. I suggest the following modifications:—(1) the specific heats should be taken at constant volume instead of at constant pressure; (2) the density of the gas should be taken as the mean of the burnt and the unburnt molecules, instead of that of the burnt molecules alone; and (3) a correction should be made for the alteration of volume by the chemical reaction, which in some cases increases, in others diminishes, the volume.

The rates so calculated agree with the explosion rates of cyanogen when burnt to carbonic oxide either by oxygen, nitrous oxide, or nitric oxide; with the explosion rates of hydrogen and oxygen with a large excess either of hydrogen, oxygen, or nitrogen; with the explosion rates of ethylene and acetylene with oxygen and a large excess of nitrogen; and, lastly, with the explosion rates of hydrogen and chlorine with an excess of hydrogen.

In conclusion, I would say that these experiments have amply confirmed the truth of Berthelot's statement that the explosion-wave is a " specific constant " for every gaseous mixture; that it has been shown that the rate of explosion depends upon the primary reaction occurring, and that the determination of the rate may throw some light on what is now so obscure—the mode in which chemical changes are brought about; and, finally, that it does not seem impossible that a connection between the rate of the molecules and the rate of the explosion may be worked out, which will give us some definite information on points of high interest in the theory of gases.

CORRESPONDENCE.

ESTIMATION OF ALUMINIUM IN IRON AND STEEL.

To the Editor of the Chemical News.

SIR,—Mr. A. S. Blackley has drawn attention to a method for the determination of aluminium in iron and steel described by me before the Society of Chemical Industry, Dec. 31, 1889, and also described by M. Carnot in your journal, pointing out that M. Carnot's method is substantially the same as mine. Practically speaking, they are identical.

I have, however, quite recently learned that although M. Carnot has never before made public his method, he claims to have taught it to his pupils for many years.

Let me point out that at the time I read my paper there was no simple method, so far as I could learn, published for the determination of minute quantities of aluminium in steel, and I explained that the process I described was simply a combination of several already well-known methods.

It gives me very great pleasure to find that other chemists, who have quite independently worked with the same object in view, should have confirmed each other. We may conclude, therefore, that the best method for determining small amounts of aluminium in steel is that described by M. Carnot and myself.—I am, &c.,

J. E. STEAD.

Laboratory and Assay Office,
5, Zetland Road, Middlesbrough,
July 30, 1891.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxiii., No. 3, July 20, 1891.

The Composition of Atmospheric Air. New Method in Weight.—A. Leduc.—the author, taking account of the relative results for the weight of a litre of air obtained by Regnault and by himself, is led to conclude that the variation in time of the weight of atmospheric air extends at most to the ten-thousandths.

On Silicon Selenide.—Paul Sabatier.—The author has obtained this compound by heating to redness crystalline silicon in a current of hydrogen selenide perfectly dry. The transformation takes place without appreciable incandescence at a temperature a little higher than the boiling-point of selenium. The selenide obtained has the form of a melted mass, hard, iridescent, of an aspect almost metallic, and does not appear to be volatile at the temperature of the experiment. Its composition is represented by the formula $SiSe_2$. Its properties resemble those of boron selenide, but being more compact it reacts much more slowly with destructive agents. Water acts very briskly, producing silica and hydrogen selenide. The total destruction of the selenide is never effected, even by prolonged immersion in hot water. Potassa produces a complete decomposition, dissolving both silica and hydrogen selenide, though a considerable time is required. Aqua regia attacks silicon selenide regularly; gelatinous silica is formed, and there remains a slight residue of silica which escapes the reaction. Silicon selenide exhales a very irritating odour, due to hydrogen selenide, formed by the moisture of the air acting upon its surface. If it is heated to dull redness in a current of dry air or oxygen, it is oxidised, forming selenious anhydride and selenium. But the combustion is only superficial.

Melting-Point of Certain Binary Organic Systems (Hydrogen Carbides).—Leo Vignon.—If we have a mixture of two definite substances, solid and fusible, not reacting chemically upon each other, in the ordinary sense of the word, and determine their melting-point, we find that it generally differs from the mean of the melting-point of the component bodies. This fact has been observed with mixtures of metals, of fusible salts, and fatty acids. The author has verified the same phenomenon in experimenting on mixtures of hydrocarbons, phenols, amines, and anhydrides, which have a melting-point, ϕ, differing from the mean, F, of the melting-points of their components.

Study of the Solid Products resulting from the Oxidation of the Drying Oils.—Ach. Livache.—When the drying oils, whether raw or having undergone an appropriate treatment, have taken up all the oxygen which they are capable of absorbing, they are found converted into a solid elastic mass, perfectly dry, and of a colour more or less brown according to the method of preparation. There is a close analogy from the physical point of view between the product of the oxidation of drying oils and caoutchouc. The author points out the prospective industrial applications of this product.

New Method of Determining Phenol.—L. Carré.—The author weighs 10 grms. of pure phenic acid, and makes up its solution to 1 litre, and with this he prepares a series of standard liquids progressively weaker at 5, 4, 3, 2, 1 grm., 0·8, 0·6, 0·4, 0·2, 0·1 grm. per litre. Suppose a solution of phenic acid. If it is concentrated it is first diluted to $\frac{1}{10}$th. Of the dilute liquid 25 c.c. are taken and introduced into a flat-bottomed flask with 5 c.c. of nitric acid. Similar portions are taken from the standard solutions, and all the flasks are placed on one and the same water-bath for one or two hours after each has received an equal admixture of nitric acid. All must be heated for exactly the same length of time. Under these conditions there are produced nitro-phenols in proportions which depend evidently on the respective quantities of the elements coming in contact. The colouration found in two experiments having the same concentration of phenol, heated for the same time and in the same manner, is always strictly equal. A preliminary examination will permit us to eliminate the standards, the colouration of which deviates too far from that of the sample under examination. To obtain further precision after the action of nitric acid at the temperature of the water-bath we add 20 c.c. of caustic soda and make up the volume to 50 c.c. We filter, if necessary, and compare the specimen with the standard which approaches nearest to it in shade with the aid of the colorimeter. The author has thus found 3·52 grms. and 0·09 grm. phenol per litre, the real quantities being 3·50 and 0·10 grm. If alcohol is present it must be driven off. Impure phenols must be heated long enough to destroy the tarry products present.

On Ozone considered from a Physiological and Therapeutic Point of View.—D. Labbé and M. Oudin.—If ozone is prepared by the chemical method it is always impure, being accompanied by highly poisonous compounds, *e.g.*, phosphorous acid. If it is prepared from pure oxygen there are obtained considerable quantities, which, being mixed with unconverted oxygen, constitute a total necessarily dangerous to breathe in a confined space. If animals are allowed to breathe in an uninclosed space, a mixture of atmospheric air and ozone, no accidents occur. Hence ozone is not dangerous to respire.

The Action of the Butyric Ferment in the Transformation of Starch into Dextrine.—A. Villiers.—The butyric ferment secretes a soluble product capable of effecting the conversion in question in the absence of any organised ferment. This product seems to be formed continuously in small proportions, and its action is rapidly exhausted as it is elaborated.

MISCELLANEOUS.

International Congress of Hygiene and Demography.—The following are the chief papers which will be read in Section V., Chemistry and Physics :—

Tuesday, August 11th.—" Town Fog and its Effects," including Smoke Prevention, introduced by Dr. W. J. Russell, F.R.S.; "On the Air of Large Towns and Methods of its Analysis," by the Manchester Field Naturalists' Society, Town Gardening Section; "The Means at our Disposal for Preventing the Emission of Smoke from Factories and Dwelling-houses," by Mr. A. E. Fletcher, H.M. Chief Inspector of Alkali Works. Dr. C. Theodore Williams will take part in the discussion with regard to Fog in Relation to Health."

Wednesday, August 12th.—" Treatment of London Sewage." by Dr. Dupré; "Outline of the Various Chemical Processes for Filtering Sewage," by Dr. J. C. Thresh ; " The Duty of a Locality to Utilise the Nitrogen of its Sewage for the Benefit of the Nation," by Dr. Alfred Carpenter ; " The Power of Soil and Vegetation Combined to Destroy Disease Germs, and so Prevent the Possibility of the Spread of Enthetic Disease in consequence of Sewage Farming," by Dr. Alfred Carpenter. Herr Stadtrath Marggraf, of Berlin, also promises a paper if unable to be present and take part in the discussion.

Thursday, August 13th.—" The Hygienic Importance of Copper," by Prof. Dr. Lehmann, of Würzburg; "The Importance to be Attached to Magnesia in Drinking Water," by Prof. P. F. Frankland, F.R.S. ; "The Action of Water on Lead," by Dr. J. H. Garrett; "The Antiseptic Treatment of Food," by Mr. Otto Hehner ; "The Effects of the Respiration of Carbonic Acid on Man," by Dr. W. Marcet, F.R.S.

Friday, August 14th.—" The Influenza and Weather of London," by Sir Arthur Mitchell and Dr. A. Buchan ; " Hygienic Improvements in the Manufacture of Bread," by Mr. J. Goodfellow, F.R.M.S. It is hoped that papers will also be contributed by Prof. Dr. O. Liebreich, of Berlin, and Prof. Dr. G. Lunge, of Zurich.

Recognition of a Fraudulent Addition of " Rubenkraut " in Rhenish Obst-Kraut.—The article known on the Rhine as " Obst-Kraut," and in Eastern Germany as Obstmuss, consists of apples, pears, or plums boiled down to a paste without the addition of sugar. It is apparently sophisticated with " Rubenkraut," a concoction of turnips. —*Zeitschrift*, xxix., Part 6.

Orsat's Apparatus for the Analysis of Chimney Gases.—This apparatus, both in its original form and in its ordinary modification, has the defect that the absorbent vessels filled with the capillary tubes is very fragile, and that the introduction and removal of these tubes is very tedious. Greiner and Friedrichs (*Zeit. Angew. Chemie*) propose a modification to obviate this defect. John Ruffle and James Mac Lachlan (*Jour. Soc. Chem. Ind.*) propose further improvements.

THE CHEMICAL NEWS.

VOL. LXIV., No. 1655.

NOTE UPON THE POWERFUL REDUCING ACTION OF SILICON.

By H. N. WARREN, Research Analyst.

METALLIC, or graphitoidal, silicon is in itself one of the most stable and inert substances with which specialists are acquainted, refusing even the oxidising influence of the oxyhydrogen flame, but strange to say that this substance, when in admixture with a large number of metallic oxides, becomes at once oxidised, the oxide in admixture with the same becoming itself reduced. Thus, for instance, if an excess of litharge be heated to dull redness only, in contact with silicon, it becomes at once reduced to metallic lead ; and, with the same facility as if carbon had been employed, when an excess of silicon is introduced a brittle regulus of silicide of lead is produced, although no such compound is obtained when these elements are heated together. With copper, and all readily reducible oxides, either a silicide or—when the oxide is in excess—the pure metal is obtained. A curious compound is obtained when a slight excess of silicon and oxide of silver are projected into a red-hot crucible ; incandescence takes place with considerable brilliance, the product formed being a semi-fluid compound, containing about 40 per cent of silicon, in appearance resembling cupric sulphide, but, unlike that substance, refusing to melt at the highest furnace temperatures, and only with difficulty when before the flame of the oxyhydrogen blowpipe.

Even metallic chromium is readily reduced by heating silicon together with the oxide of that metal, tungstic and molybdic oxides suffering a like decomposition.

A mixture of equal parts of finely-divided silicon, aluminum, and litharge, when heated together, explode with fearful violence ; in fact, so powerful is the explosive strain that I have failed to obtain any article to withstand it, which must be equal, if not superior, to fulminating silver, even cast-iron being readily shattered. The experiment is most safely performed by taking not more of the mixture than would cover a threepenny piece, supporting the same upon a stout clay-brick, and directing the flame from the blowpipe upon it : the whole generally very quickly melts, then frequently assumes a spherical condition similar to a globule of sodium. At this point it disappears with a deafening report, producing a vivid flash of light accompanied by a large volume of vapour. The surface of the brick, after the experiment, is observed to have become indented, similar to the effects observed from the detonation of nitrogen chloride.

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CONTRIBUTIONS TO THE CHEMISTRY OF ERBIUM AND DIDYMIUM.*

By GERHARD KRÜSS.
(Continued from p. 66).

IN this manner there were obtained six fractions of double sulphates, which were separately converted into nitrates by the repeated precipitation of their solutions with ammonia, by re-dissolving the precipitates (at first basic sulphates and afterwards hydroxides) in nitric acid. The absorption spectra were figured according to careful measurements made with a universal spectral apparatus adjusted for wave-lengths.

It appeared, as might be expected, that the didymium was strongly accumulated in the first fractions ; and that in the last fraction the double band Diγ at $\lambda = 579\cdot2$ and 575·4, so characteristic of didymium, are entirely wanting. In none of the fractions were the didymium lines observed without the simultaneous presence of the erbium lines, Erα at $\lambda = 654\cdot7$ was always visible, and in this manner similar results were obtained to those observed according to the method recommended (Mosander and Bunsen).

If, in separating didymium oxide from erbia, we wish to set out from the different basicity of these oxides, we may most advantageously either decompose the mixed nitrates fractionally by cautious heating, or the solution of the mixed oxides may be partially precipitated, e.g., with ammonia. The former process ranks amongst the methods most commonly used in the separation of mixed earths. Whoever has undertaken the troublesome task of decomposing considerable quantities of the nitrates by several hundreds of fractionated heatings knows how tedious is this method, and how oppressive it becomes by the continual escape of nitrous vapours.

Fractionation of the Mixed Earths with Ammonia.—It should therefore be attempted to decompose the raw material of rare earths, as obtained directly from the minerals, as far as possible by a fractionated precipitation of the neutral solution of the nitrates with very dilute ammonia. In principle such a fractionated separation of the earths from their solutions by means of ammonia is not novel ; it has been used by Cleve, Crookes, Lecoq de Boisbaudran, and others, but always merely to test the homogeneity of an earth obtained in some other manner.

Fractionation with ammonia has, in so far, the advantage over the partial decomposition of the nitrates by heat, as it furnishes in the precipitates the several earths more correctly in the serial order of their basicity. In the fractional decomposition of the earthy nitrates by heat, even if the operation is conducted in baths of known temperatures, it is difficult to keep large portions of the nitrates, when fused to pasty masses, at a uniform temperature throughout. Single portions of such melts, which come most in contact with the air, on stirring deposit themselves in crusts on the edges of the capsule and on the spatula, whilst others become more strongly heated against the sides of the capsule. On the other hand, a dilute solution of an earthy nitrate can be quickly and completely mixed with very dilute ammonia *before* a precipitation takes place, as in dilute solutions a gradual turbidity ensues only after some time, followed by the deposition of hydroxide.

Five kilos. of selected gadolinites, from Hitteroe or Ytterby, which I obtained directly from Sweden, thanks to the kindness of Herr Nilson, were ground very finely in a mill, and decomposed with hydrochloric acid by heating in large capsules. The large part of the earths present passed into solution on the first treatment with acid, whilst a small portion remained in the insoluble residue even after a second treatment with hydrochloric acid. The latter was therefore repeatedly fused with potassium hydrosulphate, the melts were treated with much water, and thus almost all the earths of the gadolinites were ultimately brought into solution. The rare earths were first precipitated from the acid solution by means of oxalic acid, and, as the supernatant solution was rich in iron, the precipitated oxalates were frequently boiled with hydrochloric acid. After drying and ignition the oxalates yielded rather more than a kilo. of the mixed rare earths.

The yellowish white oxide was completely soluble in nitric acid, and on evaporating the solution of the nitrates there was first separated out a not inconsiderable quantity of basic salts of iron and cerium, which were filtered off. The filtrate was then evaporated down several times, the residue being always taken up with water. Thus there was obtained an almost neutral solution of the

* *Liebig's Annalen.*

mixed earthy nitrates which was to be submitted to fractionated precipitation with ammonia. The absorption-spectrum of this initial solution was first closely examined with the universal spectroscope described by the author (*Ber. Deutsch. Chem. Gesell.*, xix., p. 2739), and the several lines were laid down in tables according to their relative intensities and the wave-lengths of their maximum darkness.

The fractionated precipitation was then carried out as follows :—To the solution of nitrate, previously diluted to about 20 litres, there were added at once, and with most vigorous stirring, 100 c.c. ammonia of sp. gr. 0·91, previously diluted with 2 litres water. The precipitate gradually formed settled well, and could be washed by decantation. It was filtered, and finely washed on the filters until ammonia ceased to produce a precipitate in the filtrate. Meanwhile the filtrates were again concentrated to about 20 litres, and were again fractionally precipitated with ammonia. In this manner ten fractions were obtained from the material, the neutral nitrate solutions of which yielded ten spectra. The first three fractions had nearly identical spectra, as also the fourth and fifth. Hence the erbium was accumulated in the first fractions, whilst in the spectrum of the last precipitates the erbium lines Erα (λ=654·7) and Erβ (λ=523·1) were entirely wanting, and, with the exception of a few thulium, holmium, and samarium lines, only those of didymium were present.

A second series of fractionated precipitations was then carried out with ammonia in dilute solutions, and there were obtained from the fractions—

1—3	..	..	..	..	11—18
4—5	..	..	..	..	19—25
6	..	..	..	..	26—31
7	..	..	..	..	82—35
8	..	..	..	..	36—40
9	..	..	..	..	41—46

The decomposition of the fraction of the first series was effected simultaneously, so that the fractions 11 to 46 were obtained in a relatively short time. Their absorption spectra showed that the first fractions of every new series were the richest in erbium, and that didymium passes more and more into the last precipitates of each series. Fraction 10 of the first series, when anew resolved by ammonia into five parts, gave fractions which were identical in their spectra.

It appears that, in order to undertake a third series of fractionated precipitations with ammonia, it is most advantageous to unite the fractions—

11—14, 19—21, 26—28, 32, for a material rich in erbium.

15, 16, 22, 23, 33, and 36, for a mean fraction No. 1.

17, 24, 29, 30, 34, 37, and 38, for a mean fraction No. 2.

10, 18, 25, 31, 35, 39—46, for a material rich in didymium.

The mean fractions Nos. 1 and 2 were first fractionated, the first precipitates being then mixed with the material rich in erbium, and the last precipitates with the material rich in didymium. The last two main portions were resolved by ammonia into a third series of fractionated precipitates, and so there was obtained a didymium material the most concentrated nitrate solution of which, even in a stratum 15 c.m. in thickness, no longer displayed any erbium bands in its absorption spectrum. The erbium material obtained at the same time had to be submitted to a fourth fractionation with ammonia in a very dilute solution, and the nitrate now obtained showed the erbium bands very intensely; but even in a stratum of 15 c.m. in thickness (solution of 300 grms. nitrate in 150 c.c. water) not a trace of the otherwise so intense didymium band at λ=579·2 and λ=575·4.

Such erbium and didymium materials can be obtained in a relatively very short time, as ten or more precipitates

can be obtained and worked up simultaneously. The condition for full and rapid success is washing out the ammoniacal precipitates, as thoroughly as possible, by decantation in water.

The earths obtained in this manner are still contaminated by colourless oxides, and, as the earths of ammoniacal fractionation are chiefly grouped according to basicity, didymium is chiefly accompanied by lanthanum, samarium, yttrium, and terbium, whilst erbium is chiefly accompanied by holmium, thulium, scandium, ytterbium, and cerium, provided that all these rare elements are present in the raw materials employed.

A moderately complete separation of the colourless earths of erbia and didymium was carried out *without* employing the common method of a fractionated decomposition of the nitrates of heat.

To obtain a pure didymium the following method was adopted by Dr. K. Bröckelmann (Inaugural Dissertation, Erlangen, 1891). *Beiträge zur Kentniss der Elemente der Yttrium und Cer. Gruppe.*.

In order to eliminate small quantities of cerium which still accompanied the didymium, the solution of the nitrate was mixed with a large excess of soda-lye and treated with chlorine. The hydroxides of didymium, lanthanum, and those of the colourless earths, were dissolved, whilst the residual cerium hydroxide retained but little didymium. After removing the cerium and expelling the chlorine from the filtrate, it was precipitated with ammonia, and the earthy hydrates—after being well washed—were converted into nitrates. The solution thus obtained did not give the reactions of cerium.

Hereupon the solution of didymium, almost neutral, was caused to crystallise with an excess of potassium sulphate. The rose-coloured crystalline crusts formed contained, along with didymium, a little samarium, and possibly scandium and lanthanum.

In the solution there were traces of samarium, and further of yttrium, and, if present, erbium, terbium, and ytterbium. The solution was drained away from the double sulphate by means of a filter-pump, the crystals were washed with a saturated solution of potassium sulphate, and from all the filtrates colourless hydroxide was obtained by repeated treatment with ammonia, and converted into nitric solution. The solution thus obtained displayed in its spectrum very faint samarium lines, and contained chiefly—

Yttrium (atomic weight = about 90).
Ytterbium (atomic weight = 172).
Terbium (atomic weight = about 300).

For further examination the oxide present on solution was carefully purified for the determination of its atomic weight, and on conversion into anhydrous sulphate it contained a—

$$\overset{\text{iii}}{R}=99\cdot9.$$

(*To be continued*).

CONTRIBUTIONS TO MICRO-CHEMICAL ANALYSIS.*

By H. BEHRENS.

(Continued from p. 65).

XVII.—*Barium*.

1. WITH sulphuric acid. Barium sulphate dissolves in hot concentrated sulphuric acid; it crystallises on evaporation, and cooling in rectangles of 5—12 micro., and in X-shaped skeleton crystals with right extinction. An admixture with strontium may impress upon the crystals the form of strontium sulphate (see Strontium). Limit of the reaction, 0·60005 m.grm. Ba.

Ferric chloride retards the precipitation by sulphuric

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* *Zeit. Anal. Chemie.*

acid. If much ferric chloride and hydrochloric acid are present, there are formed rhombs of 20—50 micro. with rounded angles. Chromium and aluminium chlorides have a similar effect.

2. With fluosilicates. Instead of silico-fluoric acid, as recommended by Bovicky, there may be used ammonium fluosilicate. Not too small a quantity of the reagent and of acetic acid must be used. A slow precipitation yields prisms with a dome of 40—70 micro. ; rapid precipitation produces oval leaflets and thorny globules. Strontium and calcium are not precipitated. Limit of the reaction, 0·00009 m.grm. Ba.

3. With potassium bichromate. Light yellow squares and rectangles of 10—20 micro., easily distinguished from strontium carbonate by their form. Calcium is not precipitated. Limit of the reaction, 0·00008 m.grm. Ba.

The barium solution is mixed with sodium or ammonium acetate and a sufficiency of acetic acid. Complete precipitation requires some time, but it may be accelerated by cautious heating. Compare Strontium.

4. With tartar emetic (proposed by Streng) there are obtained thin rhombs and six-sided leaflets of—

$$Ba(Sb_2O_2)C_8H_8O_{12}+2H_2O.$$
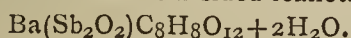
The reagent must be added to the hot solution, which should be neutral or faintly acidulated with acetic acid. Limit of the reaction. 0·00045 m.grm. Ba.

Potassium ferrocyanide, used in the same manner, gives, according to Streng, pale yellow rhombic octahedra. characteristic for barium. But calcium is precipitated by the same reagent.

Oxalic acid in presence of nitric acid throws down strontium and calcium, whilst barium is precipitated only after prolonged evaporation or the addition of sodium acetate. Boric acid and aluminium and iron chlorides retard and modify the precipitation (compare Iron). The peculiar action of stannic choride will be considered under Strontium.

Ammonium carbonate precipitates from pure solutions of barium stars of 40 micro. If strontium, calcium, or magnesium is present, the reagent is useless.

XVIII.—*Strontium.*

1. With sulphuric acid we obtain, by the procedure described under Barium, rhombs and crosses, four times as large as those of barium sulphate. The limit of this reaction is at 0·0002 m.grm. Sr. It is characteristic for strontium, since a mixture of equal parts of barium and strontium sulphates yields exclusively crystals of the form of strontium sulphate. Ferric chloride retards the precipitation. If so much iron is present that the margin of the drops appears strongly yellow during evaporation, there appear globules and rounded cubes of about 10 micro. between rods of 30 micro. Barium sulphate appears subsequently in the above-described rhombs of 20—40 micro.

2. With potassium bichromate. Neutral chromate precipitates neutral solutions of strontium salts immediately. Bichromate gives a precipitate if much sodium acetate is added. The precipitate appears the more tardily the more acetic acid is present ; more rapidly if the liquid is heated to 100°. It consists of pale yellow globules of from 20—30, or, under favourable circumstances, 100 micro. It is produced most rapidly by local supersaturation with a drop of ammonia. Limit of the reaction, 0·0008 m.grm. Sr. It is decisive in the absence of zinc.

3. With double potassium and sodium tartrate (Seignette's salt). Massive sharply-developed rhombic crystals, of the form of mispickel, isomorphous with calcium tartrate. Limit of the reaction, 0·0004 m.grm. Sr. Acetic acid retards the reaction but slightly. Barium must be previously removed, as it would carry down the strontium in the form of a powder. Calcium must not be present, as there are otherwise formed mixed crystals. Boric acid, and the aluminium, chromium, and iron chlorides occasion a granular precipitation.

4. Sodium bicarbonate precipitates, at common temperatures, radially fibrous globes, with a zonal structure and fine polarisation cross of 20—25 micro. They have so strong a double refraction that between nicols there appears a system of rings extending to the third order. Limit of the reaction, 0·0004 m.grm. Sr.

Tartar emetic gives the same reaction as barium. Oxalic acid in presence of nitric acid produces finely-developed rhombic crystals of 20—40 micro., and of an octahedral aspect. Unfortunately the reaction of oxalic acid with calcium salts is quite similar. Aluminium, chrome, and iron chlorides have little influence. The action of stannic chloride is very remarkable. If we mix an acid solution of barium, strontium, and calcium with stannic chloride, and add oxalic acid, there is first strontium precipitated in tetragonal, faintly polarising pyramids of 60—100 micro. The gradual neutralisation of the free hydrochloric acid throws down then the barium in the form of six-rayed stars of 50—120 micro., and, lastly, the calcium, which yields insignificant quadratic tables and granules of 10—25 micro. Hitherto only the crystals of the strontium compound have been closely examined. They contained, along with strontium, a considerable quantity of tin. The limit of the action is for strontium 0·0008 m.grm., for barium 0·0005 m.grm., and for calcium 0·00005 m.grm.

(To be continued).

ON SOME LECTURE EXPERIMENTS ILLUSTRATING PROPERTIES OF SALINE SOLUTIONS.*

By Prof. J. G. MACGREGOR, Dalhousie College, Halifax, N.S.

(1). IN a paper printed in the last volume of the *Proc. and Trans. N. S. Inst. Nat. Sci.* (vol. vii., 1889, p. 368), I pointed out that, according to Kohlrausch's observations, sufficiently dilute solutions of sodium hydroxide have volumes which are less than the volumes which their solvent would have in the free state, 1 grm. of a solution containing about 6 per cent of the hydroxide having a volume 0·0045 c.c. less than the water it contains. Several other substances are known which exhibit the phenomenon of contraction on solution in a similarly marked manner, but none which exhibit it to such an extent. This hydroxide, therefore, affords the best means of exhibiting the phenomenon of contraction by a lecture experiment.

The simplest mode of conducting the experiment is to pass the powdered caustic soda, little by little, down a glass tube forming a prolongation of the neck of a large bottle, the bottle and part of the tube having been first filled with distilled (or, indeed, undistilled) water. The substance is quickly dissolved by the water, the strong solution thus formed sinks and mixes with the water below, and the change of volume of the liquid is indicated by the change of height of the column of liquid in the tube. In order that the experiment may be made quickly, the powder must not be allowed to form a cake in the tube where it meets the water. To avoid this, a tube of about 7 or 8 m.m. diameter must be used. It should be several inches in length, and should have the upper end opened out to a funnel shape, to facilitate the introduction of the powder. The tube being necessarily of large bore, the bottle must also be large, so that a small change of volume may be indicated by a comparatively large elevation or depression in the tube. The hydroxide should be in the form of a powder, not only that its solution may be accomplished quickly, but also because the solution formed must be dilute in order to secure a depression of the liquid in the tube. If it be not powdered, the sub-

stance falls to the bottom and forms a strong solution there, which only gradually diffuses into the water above. Even with a fine powder, however, a comparatively strong solution is formed at the bottom. Hence I have found it advisable to catch the powder in a wire-gauze cage, attached by sealing-wax to the inner end of the rubber stopper which carries the tube, and to hasten the mixture of the strong solution, formed in the tube and cage, with the water, by diverting the downward currents of the strong solution towards the sides of the bottle by means of a plate of glass hanging horizontally below the cage. If a wide-mouthed bottle be used a stirrer may be introduced through the stopper, but leakage is thereby rendered more probable. The full amount of the contraction indicated by Kohlrausch's observations cannot of course be shown. For (1) the powdered caustic soda already contains a considerable quantity of water; (2), the solution of the substance is attended by a development of heat involving a rise of the liquid in the tube; (3), the powder carries air with it into the water, which must increase the volume whether it dissolves or remains suspended; for in the latter case, if a quick effect is desired, there is not sufficient time for it to escape up the tube; and (4), whatever precautions may be taken to secure a uniform solution throughout the bottle, it cannot be at all completely secured in the time at disposal. But notwithstanding these difficulties the experiment is a very striking one, especially if projected by a lantern on a screen. As the powdered caustic soda is passed down the tube, little by little, the liquid is seen to dissolve it without any increase in bulk, and, if the substance does not already contain too much water, with an actual diminution in bulk, the level of the liquid sinking in the tube. If the powder be added in large quantity there is a sudden rise of liquid in the tube, followed by a gradual shrinkage, which continues until the level of the liquid is lower than at the outset. The amount of the depression of the liquid in the tube is sometimes small, depending apparently upon the amount of water which the powdered caustic soda has already absorbed. The substance should not be too finely powdered, as in that case it is likely both to have taken up a considerable quantity of water and to carry down with it a considerable quantity of air. The experiment requires only a few minutes to perform.

(2). The working hypothesis which I use when thinking of the phenomena of solution has led me to the conclusion that elevation of the temperature of a solution will have, if not identically, at any rate in a general way the same effect on its selective absorption of light, and therefore on its colour, as increase in its concentration. All the experimental evidence of which I can find any record bears out this conclusion. But, whether it holds generally or not, it may be shown, by a striking lecture experiment, to hold in the case of two salts, the chlorides of cobalt ($COCl_2$) and iron ($FeCl_6$). To do so make a trough, for projection with a lantern, having thin glass sides, about the size of a lantern-slide, the glass sides being 1 or 2 m.m. from one another. It may readily be made by cutting a U-shaped piece from from a sheet of india-rubber, and cementing the glass plates to its opposite sides. Half fill the trough with a saturated solution of either salt, and fill up with a weak solution. If cobalt chloride have been used, the solution in the lower part of the trough will at ordinary temperatures be of a purplish blue, that in the upper part red; and it will be obvious that increase of the concentration of this salt involves increase of blueness in the transmitted light. If now a Bunsen flame be played carefully over one side of the trough, the solutions rapidly rise in temperature, and both are seen to increase in blueness, the saturated solution becoming deep blue and the weak solution purplish red. If the iron chloride have been used, the solution in the lower part of the trough, before heating, is seen to be of a deep orange colour, that in the upper part yellow: and it is obvious that increase in the concentration of this salt involves increase in redness. If, now, the flame be applied as before, the yellow solution

is at once seen to become orange and the orange solution red. Owing to the narrowness of the trough and the thinness of its glass sides, sufficient heating to produce a marked change of colour occupies only half a minute or so. The same trough may of course be used to project the absorption spectra of these solutions on the screen. If the slit be covered half by the one solution and half by the other, both absorption spectra may be seen at once, side by side, and the gradual variation of the spectra may be watched as the trough is gradually heated.

As a means of showing the variation of the colour or absorption spectrum of a solution with concentration, the above experiment has an obvious defect, viz., that the thickness of the layer of the strong and weak solutions being equal, the numbers of the salt molecules through which any ray of light passes are very different in the two cases. It should therefore be supplemented by showing also the colour or the spectrum obtained when the light is passed through a wide trough of the dilute solution, the ratio of the widths of the troughs being the reciprocal of the ratio of the percentages of salt in the two solutions.

(3). Dr. W. J. Nicol's observation (*Phil. Mag.*, ser. v., vol. xix., 1885, p. 453), that anhydrous sodium sulphate will dissolve in a supersaturated solution of that salt, may readily be shown as a lecture experiment by projection. For that purpose place a test-tube containing the solution in a trough with glass sides full of water, and focus it on the screen. Then let the anhydrous salt, in the form of a fine powder, fall upon the surface of the solution. By taking a pinch of the powder between the thumb and forefinger (both being quite dry) it may be made to fall as a shower of fine particles. These pass into the solution, and are seen to move slowly across the screen through the solution, dissolving as they go, in some cases disappearing, and often changing the concentration of the part of the solution through which they have passed, so as to produce obvious refraction effects. Finally, to show that the solution was supersaturated, add a few crystals of the hydrated salt, and crystallisation at once occurs. The anhydrous salt must be added as a shower of fine powder, as larger pieces may—by taking up water and forming crystals of the hydrated salt before they can dissolve—give rise to a general crystallisation of the solution.

(4). The peculiarity of the solubility in water of such substances as aniline, carbolic acid, &c., observed by Alexejew (*Wied. Ann.*, Bd. xxviii., 1886, p. 305), may readily be shown on the screen by using carbolic acid, whose critical temperature (the temperature above which it and water are mutually infinitely soluble) is about 69° C. For this purpose pour some of the acid into a long test-tube, about 12 or 15 m.m. diameter, and add water. The water will lie in a layer above the acid. Support the test-tube by a clip grasping it at the top, and focus on the screen. The line of demarcation between the two liquids will be evident. Now mix the liquids by stirring, and the whole becomes cloudy. Let the tube stand, and the liquid separates again into two layers, having different depths from those they had before, both being now solutions. As this process requires considerable time, the stirring may have been done beforehand. Next surround the test-tube by a beaker of boiling water, passing it upwards from below, and stir the liquids with a hot glass rod. A slight cloudiness appears, but the liquid quickly clears and is seen to have become homogeneous throughout, the line of demarcation having disappeared. If now the beaker of hot water be removed, and one of cold water be substituted for it, the liquid becomes cloudy, a strong solution separating out everywhere, and the little spherical masses of strong solution sinking and coalescing as they sink, to form larger spheres. After a time the liquid is seen to have again become separated into two layers. If the necessary time is not available, the separation into layers may be obtained very quickly by removing the beaker of cold water and again applying the hot bath, which, raising

the temperature, stops the separating out of the strong solution, and re-dissolves it in the surrounding weaker solution, thus producing a comparatively strong solution in the lower part of the tube and a comparatively weak one in the upper part. The experiment requires but a few minutes, and is both striking and instructive.

THE EFFECT ON BUTTER FROM FEEDING ON COTTON-SEED AND COTTON-SEED MEAL.*

By Prof. N. T. LUPTON, State Chemist.

AN investigation was undertaken a few months ago at the Alabama Experiment Station to determine the effect of cotton-seed and cotton-seed meal on the composition of the butter fat, especially on the volatile acids, the melting-point, and the specific gravity of the butter produced.

Several chemists of late years have called attention to changes produced by the use of the feed stuffs mentioned, notably Prof. Harrington, of the Texas Experiment Station, and Dr. Wiley, of the Department of Agriculture, Washington, D.C. This subject was thought to be of sufficient scientific and practical importance to justify an extended investigation. For this purpose a herd of registered Jerseys was divided into two groups, one consisting of ten cattle and the other of a single cow. The cattle of the first group were fed for a preparatory period of ten days on the customary ration used at the station, excluding cotton-seed meal and hulls; the single cow was fed on the same ration. At the end of the preparatory period, samples of milk and butter were taken for one week, on Monday, Wednesday, and Friday, and carefully analysed. The milk of the ten cattle composing the first group was mixed and churned as a whole—that of the single cow was kept separate and churned by itself. The first preparatory period was for ten days; after that, the experimental and preparatory periods extended over seven days each.

The daily rations for the different periods, which repre-

* *Journal of the American Chemical Society,* Vol. xiii., No. 4.

sent the kind and quantity of food actually consumed, were as follows:—

First period, preparatory and experimental:—

Ground oats..	5 lbs.
,, corn	5 ,,
Bran	5 ,,
Nutritive ratio	1 : 5·8.

Second period:—

Cotton-seed meal	3 lbs.
Ground oats..	4 ,,
Bran	5 ,,
Ensilage	11 ,,
Nutritive ratio..	1 : 3·75.

Third period:—

Cotton-seed meal	4 lbs.
Cotton-seed hulls	9 ,,
Ensilage	4½ ,,
Nutritive ratio..	1 : 5·08.

During the fourth period the cattle were confined exclusively to raw cotton-seed and cotton-seed hulls, and during the fifth period to cooked cotton-seed and cotton-seed hulls. They were allowed as much as they would eat. The nutritive ratios mentioned above are calculated from analyses made of the feed stuffs in use at the station. In compounding the rations, the object was not so much to conform with strictness to the German standard as to bring the cows gradually under the influence of cotton-seed, cotton-seed meal, and hulls without injury to their general health.

The results of the analysis of samples of milk and butter, taken immediately after each milking and churning, are given below. The first two tables give the composition of each sample of milk analysed, also the volatile acids, melting-point, and specific gravity of the butter from the same milk; the third table gives the average composition for each experimental period.

The following table, taken from a record carefully kept at the dairy, gives the aggregate amount of milk and

	Composition of Jersey milk for each day analysed.					Butter from same milk.			
Date.	Water.	Butter fat.	Casein.	Sugar.	Ash.	Volatile acids. Expressed in c.c. one-tenth normal alkali for 5 grms. of fat.	Melting-point.	Specific gravity at 100° C.	Rations.
Group I.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.		C.		
									Period I.
Nov. 19 ..	85·76	5·53	3·95	3·96	0·80	30·0	35·9°	0·90257	⎧ 5 lbs. ground oats.
,, 21 ..	84·95	5·20	4·05	5·09	0·81	29·6	35·3°	0·90311	⎨ 5 ,, ,, corn.
									⎩ 5 ,, bran.
									Period II.
Dec. 1 ..	84·15	5·73	4·06	5·24	0·82	29·7	36·0°	0·90411	⎧ 3 lbs. cotton-seed meal.
,, 3 ..	83·62	5·51	3·88	6·19	0·80	30·5	36·3°	0·90165	⎨ 4 lbs. ground oats.
,, 5 ..	84·26	5·16	3·90	5·98	0·80	31·4	36·1°	0·90265	⎩ 5 ,, bran. 11 lbs. ensilage.
									Period III.
Dec. 15 ..	84·53	5·96	3·64	5·12	0·75	28·4	36·6°	0·90081	⎧ 4 lbs. cotton-seed meal.
,, 17 ..	83·35	6·07	3·60	6·03	0·75	26·9	37·6°	0·90194	⎨ 9 lbs. cotton-seed hulls.
,, 19 ..	84·71	5·79	3·57	5·19	0·74	27·1	38·1°	0·90306	⎩ 4½ lbs. ensilage.
									Period IV.
Jan. 5 . ..	84·27	6·41	3·58	5·01	0·73	22·0	43·6°	0·90021	⎧ Raw cotton-seed.
,, 7 . ..	84·59	6·11	3·34	5·22	0·74	21·9	43·9°	0·89721	⎨ Cotton-seed hulls.
,, 9 . ..	84·51	5·84	3·56	5·37	0·72	22·4	43·4°	0·89955	⎩
									Period V.
Jan. 19 ..	85·84	4·87	3·39	5·16	0·74	23·1	42·7°	0·90462	⎧ Cooked cotton-seed.
,, 21 ..	84·89	5·95	3·31	5·08	0·77	22·2	42·3°	0·90057	⎨ Cotton-seed hulls.
,, 23 ..	85·38	5·53	3·31	5·04	0·74	22·1	43·0°	0·90266	⎩

	Composition of Jersey milk for each day analysed.					Butter from the same milk.			
Date.	Water.	Butter fat.	Casein.	Sugar.	Ash.	Volatile acids. Expressed in c.c. one-tenth normal alkali for 5 grms. of fat.	Melting-point. C.	Specific gravity at 100° C.	Rations.
Group II.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.				
									Period I.
Nov. 24 ..	85·53	4·67	3·84	5·23	0·73	31·4	35·1°	0·90188	{ 5 lbs. ground oats.
„ 28 ..	84·03	5·93	3·93	5·30	0·81	31·5	33·4°	0·90458	{ 5 „ „ corn. 5 lbs. bran.
									Period II.
Dec. 8 ..	85·71	4·75	3·56	5·30	0·68	—	—	—	{ 3 lbs. cotton-seed meal.
„ 10 ..	85·68	4·53	3·84	5·24	0·71	31·7	36·5°	0·90282	{ 4 lbs. ground oats.
„ 12 ..	85·63	3·94	3·66	6·02	0·75	30·6	36·2°	0·90022	5 „ bran. 11 lbs. ensilage.
									Period III.
Dec. 22 ..	85·26	4·74	3·42	5·86	0·72	25·5	37·5°	0·90192	{ 4 lbs. cotton-seed meal.
Jan. 2 . ..	84·31	5·85	3·69	5·42	0·73	25·4	41·3°	0·89798	9 lbs. cotton-seed hulls. 4½ lbs. ensilage.
									Period IV.
Jan. 12 ..	85·17	5·12	3·40	5·60	0·71	20·5	43·5°	0·89751	} Raw cotton-seed.
„ 14 ..	85·10	4·76	3·47	5·98	0·69	19·2	41·0°	0·89929	Cotton-seed hulls.
„ 16 ..	85·54	4·80	3·34	5·64	0·68	21·4	43·0°	0·89883	
									Period V.
Jan. 26 ..	86·21	4·87	3·13	5·09	0·70	22·0	43·3°	0·89775	{ Cooked cotton-seed.
„ 28 ..	86·00	4·88	3·12	5·28	0·72	22·1	43·3°	0·89994	{ Cotton-seed hulls.
„ 30 ..	85·39	6·00	3·18	4·72	0·71	21·7	44·0°	0·89803	

	Average composition of Jersey milk during each period.					Butter from same milk.			
Period. Group I.	Water.	Butter fat.	Casein.	Sugar.	Ash.	Volatile acids.	Melting-point.	Specific gravity at 100° C.	Rations.
I.	85·35	5·36	4·00	4·52	0·81	29·8	35·6°	0·90284	{ 5 lbs. each ground oats, ground corn, and bran.
II.	84·01	5·47	3·95	5·80	0·81	30·5	36·1°	0·90280	{ Cotton-seed meal, 3 lbs. ; ground oats, 4 lbs. ; bran, 5 lbs. ; ensilage, 11 lbs.
III... ..	84·20	5·91	3·60	5·45	0·75	27·5	37·4°	0·90194	{ Cotton-seed meal, 4 lbs. ; cotton-seed hulls, 9 lbs. ; ensilage, 4½ lbs.
IV... ..	84·46	6·12	3·49	5·20	0·73	22·1	43·6°	0·89899	{ Raw cotton-seed meal and cotton-seed hulls.
V.	85·37	5·45	3·36	5·09	0·75	22·5	42·7°	0·90262	{ Cooked cotton-seed meal and cotton-seed hulls.
Group II.									
I.	84·78	5·30	3·89	5·26	0·77	31·4	34·2°	0·90323	{ 5 lbs. each ground oats, ground corn, and bran.
II.	85·67	4·41	3·69	5·52	0·71	31·1	36·3°	0·90152	{ Cotton-seed meal, 3 lbs. ; ground oats, 4 lbs. ; bran, 5 lbs. ; ensilage.
III... ..	84·79	5·30	3·37	5·64	0·72	25·45	39·4°	0·89995	{ Cotton-seed meal, 4 lbs. ; cotton-seed hulls, 9 lbs. ; ensilage, 4½ lbs.
IV... ..	85·27	4·89	3·40	5·74	0·69	20·4	42·5°	0·89854	{ Raw cotton-seed meal and cotton-seed hulls.
V.	85·87	4·92	3·14	5·03	0·71	21·9	43·5°	0·89857	{ Raw cotton-seed and cotton-seed hulls.

butter produced by the first group, consisting of ten cows, for each experimental period of seven days :—

	Pounds of milk.	Pounds of butter.	Pounds of milk for one pound of butter.
Period I.	1414½	82	17·2+
„ II.	1275	85½	14·9+
„ III.	975	91	10·7+
„ IV.	896	75	11·9
„ V.	716	58	12·3+

As will be observed, there is a marked falling off in the quantity of milk, and a corresponding increase in the amount of butter produced during the first three periods, as the cattle were getting more under the influence of cotton-seed meal.

During the remaining periods the quantities of both milk and butter diminish, the ration being confined to cotton-seed and cotton-seed meal, without reference to having it well balanced as a milk ration.

The general effects of these valuable feed stuffs, when used in carefully prepared rations, will hereafter be investigated; at present we are concerned only, as previously stated, with their effects on the volatile acids, melting-point, and specific gravity of the butter fat produced under their influence. For these effects attention is called to the above tabular statements, from which the following conclusion is drawn :—

Feeding on cotton-seed and cotton-seed meal increases in a marked degree the melting-point of butter, the increase reaching in these experiments eight or nine degrees, and diminishes to a corresponding extent the volatile acids, while the specific gravity remains virtually the same.

The richness of cotton-seed meal in albumenoids renders it of prime importance to mix it with one or more feed stuffs poor in this nitrogenous compound, such as ensilage, hay, or cotton-seed hulls.

It may be stated in this connection that no change was observable in the colour of the butter from feeding cotton-seed and cotton-seed meal. The samples, still in the laboratory, are all of a beautiful golden yellow.

It is proper to state that the analytical work in the above tables was done by Dr. J. T. Anderson, first assistant in the chemical laboratory.

ELECTROLYTIC SEPARATIONS.

By EDGAR F. SMITH and FRANK MUHR.

HAVING found after many trials that gold could be completely precipitated by the current from solutions of potassio-auric cyanide, steps were taken to ascertain from what metals it could be separated. Former studies (*Amer. Chem. Jour.*, xii., 252) showed that a current of one-hundredth ampère did not precipitate palladium from a solution containing an excess of potassium cyanide until after it had acted for a period of thirty-six hours. This behaviour pointed to a possible separation of gold from palladium. These two metals were, therefore, experimented upon with the current, under the conditions indicated in the following table :—

	Gold present. Grm.	KCN. Grms.	Total dilution. c.c.	Current in c.c. OH gas per minute. C.c.	Palladium present. Grm.	Gold found. Grm.	Difference in percentage from theory.
1.	0·1162	1·50	150	0·80	0·1200	0·1162	—
2.	„	„	„	„	„	0·1163	+0·08
3.	„	„	„	„	„	0·1162	—
4.	„	„	„	„	„	0·1163	+0·08
5.	„	„	„	0·40	„	0·1160	−0·17
6.	„	„	„	„	„	0·1156	−0·52
7.	„	„	„	1·00	„	0·1164	+0·17
8.	„	„	„	„	„	0·1158	−0·34

The time allowed for the precipitation of the gold varied from twelve to fourteen hours. Cold and hot water were used for washing the precipitated metal. The deposits were made directly upon the platinum dishes. The gold was subsequently dissolved off by placing dilute potassium cyanide in the vessels, and then connecting the latter with the anode of a feeble Crowfoot battery (*Jour. Franklin Institute*, cxxxi., 300 ; *Jour. Anal. Chem.*, v., 205). The gold cyanide solution was decomposed with aqua regia, and, after obtaining gold chloride, this was carefully examined for palladium. None was discovered.

Gold from Copper.—The previous electrolytic separation of silver from copper (*Jour. Franklin Institute*, cxxix., 241) indicated that gold might perhaps be separated with equal facility from the latter metal, inasmuch as the complete deposition of the gold did not require a current much stronger than that necessary for the precipitation of silver. The separation proved successful under the conditions given below.

	Gold present. Grm.	KCN. Grm.	Total dilution. C.c.	Current in c.c. OH gas per minute. C.c.	Copper present. Grm.	Gold found. Grm.	Difference in percentage from theory.
9.	0·1725	1·5	150	0·8	0·1250	0·1725	—
10.	0·1725	3·5	„	0·4	„	0·1728	+0·17
11.	„	„	„	„	„	0·1720	−0·29
12.	„	„	„	„	„	0·1735	+0·50
13.	„	3	„	0·8	„	0·1736	+0·60

Copper was not detected in the precipitated gold. The time required for the precipitation, washing, and drying of the deposits was the same as in the separation of gold from palladium.

Gold from Cobalt.—In the electrolytic separation of mercury from cobalt, and of silver from cobalt (*Jour. Franklin Institute*, cxxix., 239, 244), satisfactory results were obtained only after the quantity of alkaline cyanide present had been reduced to 3 grms. This quantity was used in the following separations, although its increase was not accompanied by the difficulties attending the separation of the metals to which reference has just been made. Indeed, in this particular case no special effort was required in order to get satisfactory results.

	Gold present. Grm.	KCN. Grm.	Total dilution. C.c.	Current in c.c. OH gas per minute. C.c.	Cobalt present. Grm.	Gold found. Grm.	Difference in percentage from theory.
14.	0·1792	3	150	0·6	0·15—0·20	0·1789	−0·11
15.	„	„	„	„	„	0·1799	+0·49
16.	„	„	„	„	„	0·1794	+0·11
17.	„	„	„	„	„	0·1799	+0·49

The current acted upon the double cyanides through the night.

Gold from Nickel.—This separation can be made without difficulty, as is proved by the four trials given below.

	Gold present. Grm.	KCN. Grms.	Total dilution. C.c.	Current in c.c. OH gas per minute. C.c.	Nickel present. Grm.	Gold found. Grm.	Difference in percentage from theory.
18.	0·1725	2½	150	0·5	0·1373	0·1724	−0·05
19.	0·1725	3	„	1·0	„	0·1718	−0·49
20.	0·1467	2½	„	0·5	„	0·1462	−0·34
21.	„	„	„	„	„	0·1460	−0·48

The electrolytic separation of mercury from zinc in cyanide solution, as well as cadmium and silver from the latter metal, occurred without any special difficulty.

Gold from Zinc.—The current to decompose the double cyanide of zinc and potassium must yield at least 2—3 c.c. electrolytic gas per minute, so that special precautions in regard to the following separation need not be given :—

	Gold present.	KCN.	Total dilution.	Current in c.c. OH gas per minute.	Zinc present.	Gold found.	Difference in percentage from theory.
	Grm.	Grms.	C.c.	C.c.	Grm.	Grm	
22.	0·1792	3	150	0·5	0·2000	0·1796	+0·22
23.	,,	,,	,,	0·6	,,	0·1797	+0·27
24.	,,	,,	,,	,,	,,	0·1790	−0·11
25.	,,	,,	,,	,,	,,	0·1798	−0·33

It will be noticed in the preceding experiments that the gold is either slightly in excess or below the theoretical amount. This cannot be due to incomplete precipitation or to the co-precipitation of the other metal present in the double cyanide solution, for in each of the preceding cases careful search was made for all the metals operated upon ; the variations from the theoretical requirements must therefore be attributed to some other cause. The precipitations were made in platinum dishes ; these varied in weight from 60—71 grms. Care was not taken to weigh at any particular period of the day, nor were the precipitating vessels allowed any definite time for drying, &c.

The battery used to precipitate the gold consisted of 6—10 Crowfoot cells. The poles, during precipitation, were 1½ inches apart. Cover-glasses were placed over the electrolysed solution to prevent loss and to exclude dust. The latter can easily cause the metal precipitated to collect in little spongy masses, which are readily detached upon washing. To determine when the gold was fully precipitated, the level of the liquid in the dish was raised by the addition of distilled water. Before the current was finally interrupted the poles were brought more closely together, and the electrolytic action continued for a half-hour longer. It is better to do this than to remove a portion of the liquid and apply some special test to it.

It is scarcely necessary to add that if the clean platinum surface remains uncoated, the precipitation of metal is finished.

The current of the strength given in the preceding experiments *does not precipitate* platinum either from hot or from cold solution of its double cyanide when an excess of alkali cyanide is present. In this respect platinum resembles palladium. This behaviour prompted us to attempt, with good results, the separations recorded in the following lines :—

Gold from Platinum.

	Gold present.	KCN.	Total dilution.	Current in c.c. OH gas per minute.	Platinum present.	Gold found.	Difference in percentage from theory
	Grm.	Grms.		C.c.	Grm.	Grm.	
26.	0·1467	2½	150 c.c.	1	0·2433	0·1474	+0·48
27.	,,	,,	,,	,,	,,	0·1474	,,
28.	,,	,,	,,	,,	,,	0·1468	+0·05
29.	,,	,,	,,	,,	,,	0·1461	−0·40

Silver from Platinum.—In the first trials of the separation of gold from platinum the dishes were coated with a thick layer of metallic silver. When the platinum double cyanide solution was electrolysed, platinum metal was deposited upon the silver. Its precipitation was,

however, incomplete ; furthermore, silver passed into solution. This behaviour seemed to us to promise little in the way of separating silver from platinum. However, after dissolving definite amounts of salts of the two metals and adding an excess of potassium cyanide, the solution was directly electrolysed, when the silver separated upon the dish perfectly free from platinum. Currents of greater strength than that given in the recorded experiments will throw out traces of platinum. It shows itself in dark spots, distributed over the white silver surface. In such cases a black, though minute, residue will always be noticed when the precipitated silver is dissolved in dilute nitric acid. The results were as follows :—

	Silver present.	KCN.	Total dilution.	Current in c.c. OH gas per minute.	Platinum present.	Silver found.	Difference in percentage from theory.
	Grm.	Grms.	C.c.		Grm.	Grm.	
30.	0·0770	2½	150	1 c.c.	0·2433	0·0772	+0·25
31.	,,	,,	,,	,,	,,	0·0768	−0·25

Cadmium from Platinum.—Reference to a paper by Smith and Frankel (*Amer. Chem. Journ.*, xii., 428) will disclose the fact that they failed to obtain an electrolytic separation of silver and cadmium from palladium. The separation of silver from platinum succeeds if conducted under the conditions outlined in the preceding example, but the separation of cadmium from platinum resulted negatively, although the current was reduced to 0·2 c.c. oxy-hydrogen gas per minute. The precipitated cadmium always contained platinum. We also found that if the platinum dishes were coated with cadmium and the double cyanide of platinum and potassium electrolysed in these vessels, the platinum metal was deposited quite rapidly ; cadmium, however, invariably dissolved. This behaviour was similar to that observed in the attempted electrolytic separation of cadmium from palladium and from nickel.

Platinum, palladium, and nickel show many points of similarity in deportment when their double cyanide solutions are electrolysed.

Mercury from Platinum.—This separation is as readily made as that of mercury from palladium and nickel.

	Mercury present.	KCN.	Total dilution.	Current in c.c. OH gas per minute.	Platinum present.	Mercury found.	Difference in percentage from theory.
	Grm.	Grms.		C.c.	Grm.	Grm.	
32.	0·1902	2·5	150 c.c.	0·2	0·2433	0·1900	−0·10
33.	,,	,,	,,	,,	,,	0·1904	+0·10
34.	,,	,,	,,	,,	,,	0·1905	+0·15
35.	,,	,,	,,	,,	,,	0·1910	+0·41

The separations of gold, silver, and mercury from platinum were carried out in the cold. The depositions were made in the same platinum vessels used in the experiments recorded in the first part of this communication. The deposited metals were treated as mentioned in previous papers. The time of precipitation occupied from fourteen to sixteen hours.—*American Chemical Journal*, xiii., No. 6.

The Illumination of the Scale in Polarising Apparatus. — H. Schneider. — The author, instead of using a separate source of light, conducts the light of the flame which serves to illuminate the field of vision upon the scale by means of a reflecting glass rod, exactly on the principle upon which is founded the microscopic lamp of Kochs and Wolz.—*Zeitschrift*, xxix., Part 6.

SOME NOTES ON ELECTROLYTIC QUANTITATIVE SEPARATION OF METALS.

By T. O'CONNOR SLOANE, Ph.D.

IT may seem somewhat presumptuous, after Classen's classic work in electrolytic analysis, to offer any suggestions as to the conducting of this class of quantitative determinations. But there is one point in the work which, it may safely be said, has been to a certain extent neglected. This point is the influence of electromotive force, or of difference of potential upon the separations.

In Classen's work upon the subject the voltage of the circuit is duly considered, and an elaborate rheostat for regulating the voltage within somewhat crude limits (½ volt) is described. This is in one of the introductory chapters. The rheostat is for use with a 600 watt dynamo. But the author also mentions batteries, and describes his method of conducting determinations with these sources of electromotive force. The current strength is then the standard, and it is determined by the volume of oxy-hydrogen gas which the current can liberate in a definite time. In other words, the amperage of the current alone receives direct attention. By using the same sized electrodes, the author states, the conditions are kept sensibly the same. Here we have an indirect recognition of the influence of electromotive force. But the attempted maintenance of the most uniform conditions is a poor reliance. The conditions will inevitably vary and the temperature of the room and gradual change of the nature of the solution operated on, will cause variations in resistance that will affect the difference of potential. To show how little regard is paid to voltage, we are directed in iron determinations to use two and sometimes three Bunsen cells. Any change in the number of cells in series would cause great variations in the voltage, in the case cited about 50 per cent. If the cells were kept in parallel and any resistance, such as that of a voltameter, were in series with the decomposing apparatus, a great variation in voltage would even then ensue by changes in the number of cells.

The object of these notes is to plead for a greater recognition of the influence of difference of electric potential in analytical work. The facts of the case are these: For the decomposition of every solution a definite and absolutely fixed voltage is required. The strength of current affects only the condition of the deposit. Thus a current of any number of amperes might be passed through acidulated water without decomposing it until the voltage passed a fixed point, when decomposition would at once begin. A single gravity cell, large or small (sulphate of copper-zinc copper couple), cannot decompose water because its voltage is too low. The minutest bichromate cell will at once begin to decompose it, because its voltage is high enough.

Again, the amperage of the current should not be broadly stated without reference to absolutely fixed conditions of electrodes. The proper way would be to state it as referred to unit area of cathode and anode. Probably the cathode reference would be all that is needed. As ordinarily put the cathode is supposed to be a platinum dish of more or less definite size, filled with a variable depth of fluid, and the electrolytic gas set free in one or more minutes is given. All this tells nothing.

It would seem obvious that a definite and absolutely fixed difference of potential being required for the decomposition of each compound, the voltage could be made the basis for analytical work. It would be possible to effect successive separation of metals from the same solution by modifying the voltage, starting, of course, with the lowest. How far the precipitation of mixed metals, so called alloys, would interfere with such attempts is not definitely recorded. It amounts to nothing to state, as is done, that a weaker current than is required for iron or some other metals will precipitate copper. The strength of the current has nothing to do

with it. It is the difference of potential that affects the result. The varying of such difference corresponding in a general way with the strength of the current, as the operations were conducted, has doubtless occasioned the confusion.

In stating the results of, or giving directions for conducting electrolytic separations, two factors should always be stated. One is the difference of potential, the other the amperage per unit area of cathode. Then something definite would be known. It seems probably that by working on these lines some exceedingly interesting results in the way of double decompositions, as well as of separations, might be obtained.

Should any such result be obtained as the determining of a series of potential differences available for separations of metals from single solutions it would be highly interesting. The heat of combination of a vast number of compounds has been obtained and is readily reduced to volts, but such reduction is theoretical and does not accurately hold for all cases. The principal trouble would lie in the regulation of the voltage. But at the least there seems ground for research in the direction here suggested.—*Journal of the American Chemical Society*, xiii., No. 4.

FOREIGN TRADE AND METRIC WEIGHTS AND MEASURES.

FROM the Consular Report (No. 922) presented to Parliament in July, 1891, on the trade and finance of Japan, it appears that hitherto the railway plant has been mostly of English make. The locomotives, however, are chiefly made in America or Germany, and it is stated that the superior finish of French and other Continental material is now a great recommendation in the eyes of the Japanese government departments. Last, but not least, the fact that the metric scale is in use in Japan also leads to a preference being given to Continental material

We also learn that the Russian government has at last decided to make the adoption of the metric weights and measures compulsory in medical and pharmaceutical work, and it is intended that this system shall be gradually extended to all other branches of science.

There is, no doubt, a growing tendency to adopt the metric weights and measures throughout the civilised world, and it is becoming more and more important that, as a measure of self defence, if for no other reason, we should adopt them in England. In these days of keen competition with Belgian, French, German, and other foreign makers, we cannot afford to let them have the advantage of offering machines and other articles made according to the metric scale as required by so many foreign buyers, whilst we perplex them with our troublesome, unsystematised, and absurd weights and measures.

NOTICES OF BOOKS.

The Foundations of Chemistry. (Grundlagen der Chemie). Parts 3, 4, and 5. By D. MENDELEEFF, Professor at the University of St. Petersburg. Translated from the Russian by L. JAWEIN and A. THILLOT. St. Petersburg : Carl Ricker.

IN these three parts the author expounds the laws of Gay-Lussac and Avogadro, the doctrine of Berthelot, the principles of spectroscopic research, and the periodic law.

When speaking of the revelations of the spectroscope he repeats the statement that " in the universe the elementary bodies are everywhere the same as on our earth, and that—even at the high temperature which prevails in the sun—there occurs no destruction or modification of those bodies which we regard as the elements of che-

mistry." Here, again, he overlooks the increasing complexity of the spectra of the self-luminous heavenly bodies as their temperature diminishes. Moreover, those who question the absolute simplicity of our conventional elements do not assert that certain such bodies are *destroyed* by the heat of the sun, but that they are formed only when or where such heat has declined.

Prof. Mendeleeff further remarks that "the astronomer may easily fall into errors if he draws conclusions as to the composition of simple bodies from the spectra of the stars." He admits the existence of helium as possible, but he combats the views of Lockyer on the spectrum of iron as observed in the solar atmosphere. He alleges that "the concepts of the simple body and the element are in every respect better established than any results of spectroscopic investigations, that the relatively novel theory of the spectra of simple bodies is merely a result of the chemical theory of simple bodies, and that, as regards the spectroscopic phenomena, with the exception of Kirchhoff's law, no generalisations are possible which would allow us to foresee phenomena, whilst the theory of simple bodies has already reached that state." This reasoning will scarcely be accepted as conclusive by minds free from preconceptions.

The Periodic Law is naturally discussed at some length. The author states, doubtless truthfully, that the works of De Chancourtois (*vis tellurique*) and Newlands were unknown to him when he first published his researches on this subject. It seems, however, that scant justice is done to Mr. Newlands in the words that in his memoirs "some germs of the periodic law may be seen," and in placing him merely on a level with De Chancourtois whose very meaning seems to have escaped recognition in France, as well as abroad, until the appearance of M, de Boisbaudran's memoir at the beginning of the present year.

If we rightly understand the somewhat ambiguous language of Prof. Mendeleeff, he denies that Prof. Lothar Meyer had any original share in the recognition of the periodic law. The Russian *savant* considers it evident that Meyer "accepted the periodic law in the form in which I presented it."

Leaving such inquiries, we may venture to pronounce it strange that the author should so earnestly seek to uphold the simple and primordial character of the elements when his own labours have done so much to prove their genetic connection. It is, however, by no means unexampled for the discoverer of a fact or a truth to object to its results.

Prof. Mendeleeff points out that "the laws of Nature tolerate no exceptions, and differ thus from the rules, *e.g.*, of grammar." Hence spring at once the educational value of Science, and the cause of the ill-will with which it is regarded by the "humanists."

CORRESPONDENCE.

ON THE DETERMINATION OF THE AMOUNT OF FATTY MATTER PRESENT IN OLEINE (TURKEY RED OIL).

To the Editor of the Chemical News.

SIR,—Owing to absence from home I have not had an opportunity of replying to Mr. Wilson's letter (CHEMICAL NEWS, vol. lxiv., p. 49) until now. The three samples of oleine, containing definite proportions of fatty matter, referred to in my paper (CHEM. NEWS, vol. lxiv., p. 15), were made in the following manner:—First of all, the sulpho-fatty acids were prepared in the usual way from three different specimens of castor oil, and purified as thoroughly as possible by long standing in a separating-funnel, running off the bottom layer occasionally, until

no further separation took place. The sulpho-fatty acids were then left over vitriol in a desiccator for about a week. By operating in this manner the fatty matters are obtained in a practically dry state. Oleine containing any required percentage of fatty matter may then be easily prepared, all the ingredients being of course carefully weighed.

Mr. Wilson complains that I "charge him with the grave error of not comparing the ether extraction method with some standard process," but I think he has slightly misunderstood me. The meaning which I certainly intended to convey was, that it would have been better if he had tested the accuracy of his method, not against a standard *process*, but upon what may be termed a "standard *sample*" of oleine, viz., one containing a known percentage of fatty matter.—I am, &c.,

ROWLAND WILLIAMS.
Laboratory and Assay Office,
　28. Pall Mall, Manchester, Aug. 8, 1891.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxiii., No. 4, July 27, 1891.

Examination of Samples of Native Iron of Terrestrial Origin discovered in the Gold-Washings near Berezowsk.—M. Daubrée and Stanislas Meunier.—The metal is very magnetic, but manifests no polarity. Its specific gravity, determined on a specimen weighing 33·821 grms. is at 17°=7·59. A surface cut and polished is brilliant and of the ordinary colour of iron. If treated with an acid it is attacked uniformly without giving the well-known Widmannstett figures characteristic of meteoric iron. This fact, taken along with the absence of nickel, leads to the inference that this iron is not of extra terrestrial origin. Small quantities of platinum are present, probably from a mixture of ferriferous platinum with the native iron.

The Volatility of Nickel on Treatment with Hydrochloric Acid.—A. Schützenberger.—If anhydrous nickel chloride is reduced at a dull red heat with dry hydrogen gas, it is found that the hydrochloric gas escaping from the reduction-tube carries along with it sensible quantities of metal in the form of a volatile product. Special arrangements showed that this is not a case of simple mechanical transportation. The author suggests three hypotheses; the product may be a nickel hydride, which is scarcely probable, or there is formed a nickel hydrochlorate or a hydrochlorate of the chloride $NiCl_2,x(ClH)$. Iron and zinc are transported in a similar manner.

The Densities of Oxygen, Hydrogen, and Nitrogen.—A. Leduc.—The densities of the three gases are within less than 1·10,000th part—

Hydrogen	0·0695
Oxygen.	1·1050
Nitrogen	0·9720

From these values the mean centesimal proportion may be deduced as 23·235 by weight and 21·026 by volume. According to these experiments the atomic weight of nitrogen would be 13·99, and that of oxygen 15·905.

Remarks on the Transportation of Metallic Iron and Nickel by Carbon Monoxide.—Jules Garnier.—The author gives an instance of the transfer of iron observed in blast furnaces at Vierzon. Another case occurred in refining ferro-nickel on the sole of a Siemens-Martin furnace at Septèmes, where dust of metallic nickel was collected in flues which served to convey the escaping gases to a draught chimney at a considerable distance

from the furnaces. In a third case, a mixture of metallic nickel, steel, and cast iron, containing about 20 per cent of nickel, covered with a layer of flux, had been melted in a graphite crucible. When the crucible was removed from the furnace and the cover removed, there rose up a sheaf of sparks to the height of 6 metres; two-thirds of the metal were thus lost.

Action of Water upon Basic Salts of Copper.— G. Rousseau and G. Tite.—Water converts a great number of neutral metallic salts into basic salts by a process the laws of which have been discovered by M. Ditte. Some of these basic salts are brought to the state of oxides, as it occurs with antimony oxychloride and certain borates. The authors examine if the prolonged action of water at a sufficiently high temperature does not produce an analogous decomposition of other basic salts.

A Mode of the Present Formation of Mineral Sulphides.—E. Chuard.—The author, after referring to the observations of Daubrée (*Comptes Rendus*, vol. lxxx., p. 461), on the formation of mineral species in hot sulphur springs points out that mineral sulphides occur to such an extent in the superficial strata of the globe that we cannot ascribe their formation to this cause alone.

Researches on Thallium.—C. Lepierre and Lachaud —The authors have studied the action of dilute potassa upon thallium chromate, that of concentrated potassa, that of melting potassa upon thallous chromate, that of melted potassium nitrate upon the same chromate, and lastly, they have examined thallium chloro-chromate.

On the Parabanic and Oxaluric Acids.—W. C. Matignon.—The author investigates these acids from a thermo-chemical point of view.

Transformation of Gallic Acid and of Tannic into Benzoic Acid.—Ch. Er. Guignet.—A mixture of ammonia and zinc powder is placed in a flask closed with a stopper, through which passes a tube drawn out to a point. Heat is applied, and when the evolution of hydrogen is quite regular a hot solution of gallic acid is gradually added. If the temperature is kept at 60°, the gallic acid is completely transformed in a few hours. It is changed first into salicylic and then into benzoic acid. Under the same conditions tannin (digallic acid) is also converted into benzoic acid.

Acid Polymers of Ricinoleic Acid.—M. Scheurer-Kestner.—Polymerisation may be pushed as far as to the tetra- and pentaricinoleic acids. As the polymerisation advances, the acid properties of the new compounds decrease.

On Panary Fermentation.—Léon Boutroux.—Panary fermentation consists essentially in the normal alcoholic fermentation of the sugar pre-existing in the flour. The leaven produces the disengagement of gases which raise the bread, and it hinders the development of the parasitic bacteria of the flour and the water from turning the paste sour and dissolving the gluten.

Transformation of Oxycarbonated Hæmoglobine and Methæmoglobine, and on a New Method of Detecting Carbon Monoxide in Blood.—H. Bertin-Sans and J. Moitessier.—These researches contradict the conclusions of Th. Weil and B. von Anrep regarding the existence of a combination of methæmoglobine with carbon monoxide. The carbonic oxide contained in the solutions of methæmoglobine behaves exactly as if it was dissolved in water. Hence it is easy to detect minimum quantities of carbon monoxide in blood.

Zeitschrift für Analytische Chemie.
Vol. xxix., Part 6.

Determination of Sugars with Copper-Potassium Carbonate.— H. Ost.— This memoir is too long for insertion in full, and does not admit of useful abstraction.

Orsat's Apparatus for the Analysis of Chimney Gases.—(See page 74).

The Determination of Nitric and Nitrous Acids in Spring Waters.—Max Rosenfeld.—This paper will be inserted in full.

Determination of the Ignition Temperature of Explosives.—Ch. E. Monroe.—From the *Jour. Amer. Chem. Soc.*

Apparatus for Determining Carbonic Acid in Carbonates.—M. Finkener.—This paper requires the accompanying figure.

Determination of Dry Matter in Fibrous Material. —O. Knöfler (*Papier Zeitung*).—Already inserted.

Small Laboratory Appliances : Filtration with Reduced Pressure.—J. F. Stoddart.—From the *Jour. Anal. Chem.*

Treatment of Filter Paper with Nitric Acid at 1·42.—This device is successful, as the paper is not only strengthened but filters better.

A Vacuum Apparatus for Small Laboratories.— E. Dietrich (*Pharm. Central Halle*).—The air is rarefied by means of a water-pump.

Notes on Sodium Carbonate.—R. Kissling and L. Dobbin.—For the substance of this note we must refer to the *Zeit. für Angew. Chemie.*

New Determinations of the Specific Gravity of Sulphuric Acid of Different Strengths.—G. Lunge and Isler.—A series of tables.

On Lacmoid.—O. Foerster.—This paper will be inserted in full.

The Behaviour of Acids with Litmus.—J. E Marsh.—From the CHEMICAL NEWS.

On Electrolysis.—Edgar F. Smith and Lee K. Frankel.—From the *Amer. Chem. Jour.*, the *Jour. Anal. Chem.*, and the *Jour. Franklin Institute.*

A Volumetric Method for Determining Sulphuric Acid in Sulphates.—Launcelot W. Andrews.—From the *Amer. Chem. Jour.*

The Reduction of Barium Sulphate to Sulphide on Ignition with the Carbon of the Filter.—C. W. Marsh (*Jour. Anal. Chem.*).

Determination of Silica in Silicates by Fusion with Alkaline Silicates.—James P. Gilbert.—From the *Tech. Quart.*, with reference to papers on the same subject by George Craig and David Lindo (CHEMICAL NEWS).

A Modification of Elementary Analysis with Lead Chromate.—Rudolf de Roode.—From the *Amer. Chem. Jour.*

The Simultaneous Determination of Sulphur and Carbon.—L. Prunier.—From the *Comptes Rendus.*

Determination of Sulphur in Organic Substances. —W. Burton.—From the *Amer. Chem. Jour.*

Determination of Acetone in Wood Spirit.—L. Vignon and G. Arachequesne.—From th *Comptes Rendus.*

THE CHEMICAL NEWS.

Vol. LXIV., No. 1656.

BRITISH ASSOCIATION

FOR THE

ADVANCEMENT OF SCIENCE.

Cardiff, 1891.

ADDRESS OF THE PRESIDENT,

William Huggins, Esq.,
D.C.L. (Oxon.), LL.D. (Cantab., Edin., et Dubl.),
Ph.D. (Lugd. Bat.), F.R.S., F.R.A.S., Hon. F.R.S.E., &c.,
Correspondant de l'Institut de France.

It is now many years since this Association has done honour to the science of Astronomy in the selection of its President.

Since Sir George Airy occupied the Chair in 1851, and the late Lord Wrottesley nine years later in 1860, other sciences have been represented by the distinguished men who have presided over your meetings.

The very remarkable discoveries in our knowledge of the heavens which have taken place during this period of thirty years—one of amazing and ever-increasing activity in all branches of science—have not passed unnoticed in the addresses of your successive Presidents; still it seems to me fitting that I should speak to you to-night chiefly of those newer methods of astronomical research which have led to those discoveries, and which have become possible by the introduction since 1860 into the observatory of the spectroscope and the modern photographic plate.

In 1866 I had the honour of bringing before this Association, at one of the evening lectures, an account of the first-fruits of the novel and unexpected advances in our knowledge of the celestial bodies which followed rapidly upon Kirchhoff's original work on the solar spectrum and the interpretation of its lines.

Since that time a great harvest has been gathered in the same field by many reapers. Spectroscopic astronomy has become a distinct and acknowledged branch of the science, possessing a large literature of its own and observatories specially devoted to it. The more recent discovery of the gelatine dry plate has given a further great impetus to this modern side of astronomy, and has opened a pathway into the unknown of which even an enthusiast thirty years ago would scarcely have dared to dream.

In no science, perhaps, does the sober statement of the results which have been achieved appeal so strongly to the imagination, and make so evident the almost boundless powers of the mind of man. By means of its light alone to analyse the chemical nature of a far distant body; to be able to reason about its present state in relation to the past and future; to measure within an English mile or less per second the otherwise invisible motion which it may have towards or from us; to do more, to make even that which is darkness to our eyes light, and from vibrations which our organs of sight are powerless to perceive to evolve a revelation in which we see mirrored some of the stages through which the stars may pass in their slow evolutional progress—surely the record of such achievements, however poor the form of words in which they may be described, is worthy to be regarded as the scientific epic of the present century.

I do not purpose to attempt a survey of the progress of spectroscopic astronomy from its birth at Heidelberg in 1859, but to point out what we do know at present, as distinguished from what we do not know, of a few only of its more important problems, giving a prominent place, in accordance with the traditions of this chair, to the work of the last year or two.

In the spectroscope itself advances have been made by Lord Rayleigh by his discussion of the theory of the instrument, and by Professor Rowland in the construction of concave gratings.

Lord Rayleigh has shown that there is not the necessary connection, sometimes supposed, between dispersion and resolving power, as besides the prism or grating other details of construction and of adjustment of a spectroscope must be taken into account.

The resolving power of the prismatic spectroscope is proportional to the length of path in the dispersive medium. For the heavy flint glass used in Lord Rayleigh's experiments the thickness necessary to resolve the sodium lines came out 1·02 c.m. If this be taken as a unit the resolving power of a prism of similar glass will be in the neighbourhood of the sodium lines equal to the number of c.m. of its thickness. In other parts of the spectrum the resolving power will vary inversely as the third power of the wave-length, so that it will be eight times as great in the violet as in the red. The resolving power of a spectroscope is therefore proportional to the total thickness of the dispersive material in use, irrespective of the number, the angles, or the setting of the separate prisms into which, for the sake of convenience, it may be distributed.

The resolving power of a grating depends upon the total number of lines on its surface and the order of spectrum in use, about 1000 lines being necessary to resolve the sodium lines in the first spectrum.

As it is often of importance in the record of observations to state the efficiency of the spectroscope with which they were made, Professor Schuster has proposed the use of a unit of purity as well as of resolving power, for the full resolving power of a spectroscope is realised in practice only when a sufficiently narrow slit is used. The unit of purity also is to stand for the separation of two lines differing by one-thousandth of their own wavelength; about the separation of the sodium pair at D.

A further limitation may come in from the physiological fact that, as Lord Rayleigh has pointed out, the eye when its full aperture is used is not a perfect instrument. If we wish to realise the full resolving power of a spectroscope, therefore, the emergent beam must not be larger than about one-third of the opening of the pupil.

Up to the present time the standard of reference for nearly all spectroscopic work continues to be Ångström's map of the solar spectrum, and his scale based upon his original determinations of absolute wave-length. It is well known, as was pointed out by Thalén in his work on the spectrum of iron in 1884, that Ångström's figures are slightly too small in consequence of an error existing in a standard metre used by him. The corrections for this have been introduced into the tables of the wave-lengths of terrestrial spectra collected and revised by a Committee of this Association from 1885 to 1887. Last year the Committee added a table of corrections to Rowland's scale.

The inconvenience caused by a change of standard scale is, for a time at least, considerable; but there is little doubt that in the near future Rowland's photographic map of the solar spectrum, and his scale based on the determinations of absolute wave-length by Pierce and Bell, or the Potsdam scale based on original determinations by Müller and Kempf, which differs very slightly from it, will come to be exclusively adopted.

The great accuracy of Rowland's photographic map is due chiefly to the introduction by him of concave gratings, and of a method for their use, by which the problem of the determination of relative wave-lengths is simplified to measures of coincidences of the lines in different spectra by a micrometer.

The concave grating and its peculiar mounting, in which no lenses or telescope are needed, and in which all

the spectra are in focus together, formed a new departure of great importance in the measurement of spectral lines. The valuable method of photographic sensitisers for different parts of the spectrum has enabled Professor Rowland to include in his map the whole visible solar spectrum, as well as the ultra-violet portion as far as it can get through our atmosphere. Some recent photographs of the solar spectrum, which include A, by Mr. George Higgs, are of great technical beauty.

During the past year the results of three independent researches have appeared, in which the special object of the observers has been to distinguish the lines which are due to our atmosphere from those which are truly solar—the maps of M. Thollon, which, owing to his lamented death just before their final completion, have assumed the character of a memorial of him; maps by Dr. Becker; and sets of photographs of a high and a low sun by Mr. McClean.

At the meeting of this Association in Bath, M. Janssen gave an account of his own researches on the terrestrial lines of the solar spectrum, which owe their origin to the oxygen of our atmosphere. He discovered the remarkable fact that while one class of bands varies as the density of the gas, other diffuse bands vary as the square of the density. These observations are in accordance with the work of Egoroff and of Olszewski, and of Liveing and Dewar on condensed oxygen. In some recent experiments Olszewski, with a layer of liquid oxygen 30 m.m. thick, saw, as well as four other bands, the band coincident with Fraunhofer's A—a remarkable instance of the persistence of absorption through a great range of temperature. The light which passed through the liquid oxygen had a light blue colour resembling that of the sky. Of not less interest are the experiments of Knut Ångström, which show that the carbonic acid and aqueous vapour of the atmosphere reveal their presence by dark bands in the invisible infra-red region, at the positions of bands of emission of these substances.

It is now some thirty years since the spectroscope gave us for the first time certain knowledge of the nature of the heavenly bodies, and revealed the fundamental fact that terrestrial matter is not peculiar to the solar system, but is common to all the stars which are visible to us.

In the case of a star such as Capella, which has a spectrum almost identical with that of the sun, we feel justified in concluding that the matter of which it is built up is similar, and that its temperature is also high, and not very different from the solar temperature. The task of analysing the stars and nebulæ becomes, however, one of very great difficulty when we have to do with spectra differing from the solar type. We are thrown back upon the laboratory for the information necessary to enable us to interpret the indications of the spectroscope as to the chemical nature, the density and pressure, and the temperature of the celestial masses.

What the spectroscope immediately reveals to us are the waves which were set up in the ether filling all interstellar space, years or hundreds of years ago, by the motions of the molecules of the celestial substances. As a rule it is only when a body is gaseous and sufficiently hot that the motions within its molecules can produce bright lines and a corresponding absorption. The spectra of the heavenly bodies are, indeed, to a great extent absorption spectra, but we have usually to study them through the corresponding emission spectra of bodies brought into the gaseous form and rendered luminous by means of flames or of electric discharges. In both cases, unfortunately, as has been shown recently by Professors Liveing and Dewar, Wüllner, E. Wiedemann, and others, there appears to be no certain direct relation between the luminous radiation as shown in the spectroscope and the temperature of the flame, or of the gaseous contents of the vacuum tube—that is, in the usual sense of the term as applied to the mean motion of all the molecules. In both cases the vibratory motions within the molecules to

which their luminosity is due are almost always much greater than would be produced by encounters of molecules having motions of translation no greater than the average motions which characterise the temperature of the gases as a whole. The temperature of a vacuum tube through which an electric discharge is taking place may be low, as shown by a thermometer, quite apart from the consideration of the extreme smallness of the mass of gas; but the vibrations of the luminous molecules must be violent in whatever way we suppose them to be set up by the discharge. If we take Schuster's view, that comparatively few molecules are carrying the discharge, and that it is to the fierce encounters of these alone that the luminosity is due, then if all the molecules had similar motions the temperature of the gas would be very high.

So in flames where chemical changes are in progress, the vibratory motions of the molecules which are luminous may be, in connection with the energy set free in these changes, very different from those corresponding to the mean temperature of the flame.

Under the ordinary conditions of terrestrial experiments, therefore, the temperature or the mean vis viva of the molecules may have no direct relation to the total radiation, which, on the other hand, is the sum of the radiation due to each luminous molecule.

These phenomena have recently been discussed by Ebert from the standpoint of the electro-magnetic theory of light.

Very great caution is therefore called for when we attempt to reason by the aid of laboratory experiments to the temperature of the heavenly bodies from their radiation, especially on the reasonable assumption that in them the luminosity is not ordinarily associated with chemical changes or with electrical discharges, but is due to a simple glowing from the ultimate conversion into molecular motion of the gravitational energy of shrinkage.

In a recent paper Stas maintains that electric spectra are to be regarded as distinct from flame spectra and from researches of his own; that the pairs of lines of the sodium spectrum other than D are produced only by disruptive electric discharges. As these pairs of lines are found reversed in the solar spectrum, he concludes that the sun's radiation is due mainly to electric discharges. But Wolf and Diacon, and later, Watts, observed the other pairs of lines of the sodium spectrum when the vapour was raised above the ordinary temperature of the Bunsen flame. Recently Liveing and Dewar saw easily, besides D, the citron and green pairs, and sometimes the blue pair and the orange pair, when hydrogen charged with sodium vapour was burning at different pressures in oxygen. In the case of sodium vapour, therefore, and presumably in all other vapours and gases, it is a matter of indifference whether the necessary vibratory motion of the molecules is produced by electric discharges or by flames. The presence of lines in the solar spectrum which we can only produce electrically is an indication, however, as Stas points out, of the high temperature of the sun.

We must not forget that the light from the heavenly bodies may consist of the combined radiations of different layers of gas at different temperatures, and possibly be further complicated to an unknown extent by the absorption of cooler portions of gas outside.

Not less caution is needed if we endeavour to argue from the broadening of lines and the coming in of a continuous spectrum as to the relative pressure of the gas in the celestial atmospheres. On the one hand it cannot be gainsaid that in the laboratory the widening of the lines in a Plücker's tube follows upon increasing the density of the residue of hydrogen in the tube, when the vibrations are more frequently disturbed by fresh encounters, and that a broadening of the sodium lines in a flame at ordinary pressure is produced by an increase of the quantity of sodium in the flame; but it is doubtful if pressure, as distinguished from quantity, does produce an increase of the breadth of the lines. An individual molecule of sodium will be sensibly in the same condition,

considering the relatively enormous number of the molecules of the other gases, whether the flame is scantily or copiously fed with the sodium salt. With a small quantity of sodium vapour the intensity will be feeble, except near the maximum of the lines; when, however, the quantity is increased, the comparative transparency on the sides of the maximum will allow the light from the additional molecules met with in the path of the visual ray to strengthen the radiation of the molecules farther back, and so increase the breadth of the lines.

In a gaseous mixture it is found, as a rule, that at the same pressure or temperature, as the encounters with similar molecules become fewer, the spectral lines will be affected as if the body were observed under conditions of reduced quantity or temperature.

In their recent investigation of the spectroscopic behaviour of flames under various pressures up to forty atmospheres, Professors Liveing and Dewar have come to the conclusion that though the prominent feature of the light emitted by flames at high pressure appears to be a strong continuous spectrum, there is not the slightest indication that this continuous spectrum is produced by the broadening of the lines of the same gases at low pressure. On the contrary, photometric observations of the brightness of the continuous spectrum, as the pressure is varied, show that it is mainly produced by the mutual action of the molecules of a gas. Experiments on the sodium spectrum were carried up to a pressure of forty atmospheres without producing any definite effect on the width of the lines which could be ascribed to the pressure. In a similar way the lines of the spectrum of water showed no signs of expansion up to twelve atmospheres; though more intense than at ordinary pressure, they remained narrow and clearly defined.

It follows, therefore, that a continuous spectrum cannot be considered, when taken alone, as a sure indication of matter in the liquid or the solid state. Not only, as in the experiments already mentioned, such a spectrum may be due to gas when under pressure, but, as Maxwell pointed out, if the thickness of a medium, such as sodium vapour, which radiates and absorbs different kinds of light, be very great, and the temperature high, the light emitted will be of exactly the same composition as that emitted by lamp-black at the same temperature, for the radiations which are feebly emitted will be also feebly absorbed, and can reach the surface from immense depths. Schuster has shown that oxygen, even in a partially exhausted tube, can give a continuous spectrum when excited by a feeble electric discharge.

Compound bodies are usually distinguished by a banded spectrum; but on the other hand such a spectrum does not necessarily show the presence of compounds, that is, of molecules containing different kinds of atoms, but simply of a more complex molecule, which may be made up of similar atoms, and be therefore an allotropic condition of the same body. In some cases, for example, in the diffuse bands of the absorption spectrum of oxygen, the bands may have an intensity proportional to the square of the density of the gas, and may be due either to the formation of more complex molecules of the gas with increase of pressure, or it may be to the constraint to which the molecules are subject during their encounters with one another.

It may be thought that at least in the coincidences of bright lines we are on the solid ground of certainty, since the length of the waves set up in the ether by a molecule, say of hydrogen, is the most fixed and absolutely permanent quantity in nature, and is so of physical necessity, for with any alteration the molecule would cease to be hydrogen.

Such would be the case if the coincidence were certain; but an absolute coincidence can be only a matter of greater or less probability, depending on the resolving power employed, on the number of the lines which correspond, and on their characters. When the coincidences are very numerous, as in the case of iron and the solar spectrum, or the lines are characteristically grouped, as in the case of hydrogen and the solar spectrum, we may regard the coincidence as certain; but the progress of science has been greatly retarded by resting important conclusions upon the apparent coincidence of single lines, in spectroscopes of very small resolving power. In such cases, unless other reasons supporting the coincidence are present, the probability of a real coincidence is almost too small to be of any importance, especially in the case of a heavenly body which may have a motion of approach or of recession of unknown amount.

But even here we are met by the confusion introduced by multiple spectra, corresponding to different molecular groupings of the same substance; and, further, to the influence of substances in vapour upon each other; for when several gases are present together, the phenomena of radiation and reversal by absorption are by no means the same as if the gases were free from each other's influence, and especially is this the case when they are illuminated by an electric discharge.

I have said as much as time will permit, and I think indeed sufficient, to show that it is only by the laborious and slow process of most cautious observation that the foundations of the science of celestial physics can be surely laid. We are at present in a time of transition when the earlier, and, in the nature of things, less precise observations are giving place to work of an order of accuracy much greater than was formerly considered attainable with objects of such small brightness as the stars.

The accuracy of the earlier determinations of the spectra of the terrestrial elements are in most cases insufficient for modern work on the stars as well as on the sun. They fall much below the scale adopted in Rowland's map of the sun, as well as below the degree of accuracy attained at Potsdam by photography in a part of the spectrum for the brighter stars. Increase of resolving power very frequently breaks up into groups, in the spectra of the sun and stars, the lines which had been regarded as single, and their supposed coincidences with terrestrial lines fall to the ground. For this reason many of the early conclusions, based on observation as good as it was possible to make at the time with the less powerful spectroscopes then in use, may not be found to be maintained under the much greater resolving power of modern instruments.

The spectroscope has failed as yet to interpret for us the remarkable spectrum of the Aurora Borealis. Undoubtedly in this phenomenon portions of our atmosphere are lighted up by electric discharges; we should expect, therefore, to recognise the spectra of the gases known to be present in it. As yet we have not been able to obtain similar spectra from these gases artificially, and especially we do not know the origin of the principal line in the green, which often appears alone, and may have therefore an origin independent of that of the other lines. Recently the suggestion has been made that the Aurora is a phenomenon produced by the dust of meteors and falling stars, and that near positions of certain auroral lines to lines or flutings of manganese, lead, barium, thallium, iron, &c., are sufficient to justify us in regarding meteoric dust in the atmosphere as the origin of the auroral spectrum. Liveing and Dewar have made a conclusive research on this point, by availing themselves of the dust of excessive minuteness thrown off from the surface of electrodes of various metals and meteorites by a disruptive discharge, and carried forward into the tube of observation by a more or less rapid current of air or other gas. These experiments prove that metallic dust, however fine, suspended in a gas will not act like gaseous matter in becoming luminous with its characteristic spectrum in an electric discharge, similar to that of the Aurora. Professor Schuster has suggested that the principal line may be due to some very light gas which is present in too small a proportion to be detected by chemical analysis, or even by the spectroscope in the

presence of the other gases near the earth, but which, at the height of the auroral discharges, is in a sufficiently greater relative proportion to give a spectrum. Lemström, indeed, states that he saw this line in the silent discharge of a Holtz machine on a mountain in Lapland. The lines may not have been obtained in our laboratories from the atmospheric gases, on account of the difficulty of reproducing in tubes with sufficient nearness the conditions under which the auroral discharges take place.

In the spectra of comets the spectroscope has shown the presence of carbon presumably in combination with hydrogen, and also sometimes with nitrogen; and in the case of comets approaching very near the sun, the lines of sodium, and other lines which have been supposed to belong to iron. Though the researches of Professor H. A. Newton and of Professor Schiaparelli leave no doubt of the close connection of comets with corresponding periodic meteor swarms, and therefore of the probable identity of cometary matter with that of meteorites, with which the spectroscopic evidence agrees, it would be perhaps unwise at present to attempt to define too precisely the exact condition of the matter which forms the nucleus of the comet. In any case the part of the light of the comet, which is not reflected solar light, can scarcely be attributed to a high temperature produced by the clashing of separate meteoric stones set up within the nucleus by the sun's disturbing force. We must look rather to disruptive electric discharges produced probably by processes of evaporation due to increased solar heat, which would be amply sufficient to set free portions of the occluded gases into the vacuum of space. May it be that these discharges are assisted, and indeed possibly increased, by the recently discovered action of the ultra-violet part of the sun's light? Lenard and Wolf have shown that ultra-violet light can produce a discharge from a negatively electrified piece of metal, while Hallwachs and Righi have shown further that ultra-violet light can even charge positively an unelectrified piece of metal. Similar actions on cometary matter, unscreened as it is by an absorptive atmosphere, at least of any noticeable extent, may well be powerful when a comet approaches the sun, and help to explain an electrified condition of the evaporated matter which would possibly bring it under the sun's repulsive action. We shall have to return to this point in speaking of the solar corona.

A very great advance has been made in our knowledge of the constitution of the sun by the recent work at the Johns Hopkins University by means of photography and concave gratings, in comparing the solar spectrum. under great resolving power, directly with the spectra of the terrestrial elements. Professor Rowland has shown that the lines of thirty-six terrestrial elements at least are certainly present in the solar spectrum, while eight others are doubtful. Fifteen elements, including nitrogen, as it shows itself under an electric discharge in a vacuum tube, have not been found in the solar spectrum. Some ten other elements, inclusive of oxygen, have not yet been compared with the sun's spectrum.

Rowland remarks that of the fifteen elements named as not found in the sun, many are so classed because they have few strong lines, or none at all, in the limit of the solar spectrum as compared by him with the arc. Boron has only two strong lines. The lines of bismuth are compound and too diffuse. Therefore, even in the case of these fifteen elements, there is little evidence that they are really absent from the sun.

It follows that if the whole earth were heated to the temperature of the sun, its spectrum would resemble very closely the solar spectrum.

Rowland has not found any lines common to several elements, and in the case of some accidental coincidences, more accurate investigation reveals some slight difference of wave-length or a common impurity. Further, the relative strength of the lines in the solar spectrum is generally, with a few exceptions, the same as that in the electric arc, so that Rowland considers that his experi-

ments show "very little evidence" of the breaking up of the terrestrial elements in the sun.

Stas, in a recent paper, gives the final results of eleven years of research on the chemical elements in a state of purity, and on the possibility of decomposing them by the physical and chemical forces at our disposal. His experiments on calcium, strontium, lithium, magnesium, silver, sodium, and thallium, show that these substances retain their individuality under all conditions, and are unalterable by any forces that we can bring to bear upon them.

Professor Rowland looks to the solar lines which are unaccounted for as a means of enabling him to discover such new terrestrial elements as still lurk in rare minerals and earths, by confronting their spectra directly with that of the sun. He has already resolved yttrium spectroscopically into three components, and actually into two. The comparison of the results of this independent analytical method with the remarkable but different conclusions to which M. Lecoq de Boisbaudran and Mr. Crookes have been led respectively, from spectroscopic observation of these bodies when glowing under molecular bombardment in a vacuum tube, will be awaited with much interest. It is worthy of remark that as our knowledge of the spectrum of hydrogen in its complete form came to us from the stars, it is now from the sun that chemistry is probably about to be enriched by the discovery of new elements.

In a discussion in the Bakerian lecture for 1885 of what we knew up to that time of the sun's corona, I was led to the conclusion that the corona is essentially a phenomenon similar in the cause of its formation to the tails of comets, namely, that it consists for the most part probably of matter going from the sun under the action of a force, possibly electrical, which varies as the surface, and can therefore in the case of highly attenuated matter, easily master the force of gravity even near the sun. Though many of the coronal particles may return to the sun, those which form the long rays or streamers do not return; they separate, and soon become too diffused to be any longer visible, and may well go to furnish the matter of the zodiacal light, which otherwise has not received a satisfactory explanation. And further, if such a force exist at the sun, the changes of terrestrial magnetism may be due to direct electric action, as the earth moves through lines of inductive force.

These conclusions appear to be in accordance broadly with the lines along which thought has been directed by the results of subsequent eclipses. Professor Schuster takes an essentially similar view, and suggests that there may be a direct electric connection between the sun and the planets. He asks further whether the sun may not act like a magnet in consequence of its revolution about its axis. Professor Bigelow has recently treated the coronal forms by the theory of spherical harmonics, on the supposition that we see phenomena similar to those of free electricity, the rays being lines of force, and the coronal matter discharged from the sun, or at least arranged or controlled by these forces. At the extremities of the streams for some reasons the repulsive power may be lost, and gravitation set in, bringing the matter back to the sun. The matter which does leave the sun is persistently transported to the equatorial plane of the corona; in fact, the zodiacal light may be the accumulation at great distances from the sun along this equator of such like material. Photographs on a larger scale will be desirable for the full development of the conclusions which may follow from this study of the curved forms of the coronal structure. Professor Schaeberle, however, considers that the coronal phenomena may be satisfactorily accounted for on the supposition that the corona is formed of streams of matter ejected mainly from the spot zones with great initial velocities, but smaller than 382 miles a second. Further, that the different types of the corona are due to the effects of perspective on the streams from the earth's place at the time relatively to the plane of the solar equator.

Of the physical and the chemical nature of the coronal matter we know very little. Schuster concludes, from an examination of the eclipses of 1882, 1883, and 1886, that the continuous spectrum of the corona has the maximum of actinic intensity displaced considerably towards the red when compared with the spectrum of the sun, which shows that it can only be due in small part to solar light scattered by small particles. The lines of calcium and of hydrogen do not appear to form part of the normal spectrum of the corona. The green coronal line has no known representative in terrestrial substances, nor has Schuster been able to recognise any of our elements in the other lines of the corona.

The spectra of the stars are almost infinitely diversified, yet they can be arranged with some exceptions in a series in which the adjacent spectra, especially in the photographic region, are scarcely distinguishable, passing from the bluish-white stars like Sirius, through stars more or less solar in character, to stars with banded spectra, which divide themselves into two apparently independent groups according as the stronger edge of the bands is towards the red or the blue. In such an arrangement the sun's place is towards the middle of the series.

At present a difference of opinion exists as to the direction in the series in which evolution is proceeding, whether by further condensation white stars pass into the orange and red stages, or whether these more coloured stars are younger, and will become white by increasing age. The latter view was suggested by Johnstone Stoney in 1867.

About ten years ago Ritter, in a series of papers, discussed the behaviour of gaseous masses during condensation, and the probable resulting constitution of the heavenly bodies. According to him a star passes through the orange and red stages twice, first during a comparatively short period of increasing temperature which culminates in the white stage, and a second time during a more prolonged stage of gradual cooling. He suggested that the two groups of banded stars may correspond to these different periods: the young stars being those in which the stronger edge of the dark band is towards the blue, the other banded stars, which are relatively less luminous and few in number, being those which are approaching extinction through age.

Recently a similar evolutional order has been suggested, which is based upon the hypothesis that the nebulæ and stars consist of colliding meteoric stones in different stages of condensation.

More recently the view has been put forward that the diversified spectra of the stars do not represent the stages of an evolutional progress, but are due for the most part to differences of original constitution.

The few minutes which can be given to this part of the address are insufficient for a discussion of these different views. I purpose, therefore, to state briefly, and with reserve as the subject is obscure, some of the considerations from the characters of their spectra which appeared to me to be in favour of the evolutional order in which I arranged the stars from their photographic spectra in 1879. This order is essentially the same as Vogel had previously proposed in his classification of the stars in 1874, in which the white stars, which are most numerous, represent the early adult and most persistent stage of stellar life, the solar condition that of full maturity and of commencing age; while in the orange and red stars with banded spectra we see the setting in and advance of old age. But this statement must be taken broadly, and not as asserting that all stars, however different in mass and possibly to some small extent in original constitution, exhibit one invariable succession of spectra.

In the spectra of the white stars the dark metallic lines are relatively inconspicuous, and occasionally absent, at the same time that the dark lines of hydrogen are usually strong, and more or less broad, upon a continuous spectrum, which is remarkable for its brilliancy at the blue end. In

some of these stars the hydrogen and some other lines are bright, and sometimes variable.

As the greater or less prominence of the hydrogen lines, dark or bright, is characteristic of the white stars as a class, and diminishes gradually with the incoming and increase in strength of the other lines, we are probably justified in regarding it as due to some conditions which occur naturally during the progress of stellar life, and not to a peculiarity of original constitution.

To produce a strong absorption-spectrum a substance must be at the particular temperature at which it is notably absorptive; and, further, this temperature must be sufficiently below that of the region behind from which the light comes for the gas to appear, so far as its special rays are concerned, as darkness upon it. Considering the high temperature to which hydrogen must be raised before it can show its characteristic emission and absorption, we shall probably be right in attributing the relative feebleness or absence of the other lines, not to the paucity of the metallic vapours, but rather to their being so hot relatively to the substances behind them as to show feebly, if at all, by reversion. Such a state of things would more probably be found, it seems to me, in conditions anterior to the solar stage. A considerable cooling of the sun would probably give rise to banded spectra due to compounds, or to more complex molecules, which might form near the condensing points of the vapours.

The sun and stars are generally regarded as consisting of glowing vapours surrounded by a photosphere where condensation is taking place, the temperature of the photospheric layer from which the greater part of the radiation comes being constantly renewed from the hotter matter within.

At the surface the convection currents would be strong, producing a considerable commotion, by which the different gases would be mixed and not allowed to retain the inequality of proportions at different levels due to their vapour densities.

Now the conditions of the radiating photosphere and those of the gases above it, on which the character of the spectrum of a star depends, will be determined, not alone by temperature, but also by the force of gravity in these regions; this force will be fixed by the star's mass and its stage of condensation, and will become greater as the star continues to condense.

In the case of the sun the force of gravity has already become so great at the surface that the decrease of the density of the gases must be extremely rapid, passing in the space of a few miles from atmospheric pressure to a density infinitesimally small; consequently the temperature gradient at the surface, if determined solely by expansion, must be extremely rapid. The gases here, however, are exposed to the fierce radiation of the sun, and unless wholly transparent would take up heat, especially if any solid or liquid particles were present from condensation or convection currents.

From these causes, within a very small extent of space at the surface of the sun, all bodies with which we are acquainted should fall to a condition in which the extremely tenuous gas could no longer give a visible spectrum. The insignificance of the angle subtended by this space as seen from the earth should cause the boundary of the solar atmosphere to appear defined. If the boundary which we see be that of the sun proper, the matter above it will have to be regarded as in an essentially dynamical condition—an assemblage, so to speak, of gaseous projectiles for the most part falling back upon the sun after a greater or less range of flight. But in any case it is within a space of relatively small extent in the sun, and probably in the other solar stars, that the reversion which is manifested by dark lines is to be regarded as taking place.

Passing backward in the star's life, we should find a gradual weakening of gravity at the surface, a reduction of the temperature gradient so far as it was determined by expansion, and convection currents of less violence

producing less interference with the proportional quanti-ties of gases due to their vapour densities, while the effects of eruptions would be more extensive.

At last we might come to a state of things in which, if the star were hot enough, only hydrogen might be suffi-ciently cool relatively to the radiation behind to produce a strong absorption. The lower vapours would be pro-tected, and might continue to be relatively too hot for their lines to appear very dark upon the continuous spectrum ; besides, their lines might be possibly to some extent effaced by the coming in under such conditions in the vapours themselves of a continuous spectrum.

In such a star the light radiated towards the upper part of the atmosphere may have come from portions lower down of the atmosphere itself, or at least from parts not greatly hotter. There may be no such great difference of temperature of the low and less low portions of the star's atmosphere as to make the darkening effect of absorption of the protected metallic vapours to prevail over the illuminating effect of their emission.

It is only by a vibratory motion corresponding to a very high temperature that the bright lines of the first spectrum of hydrogen can be brought out, and by the equivalence of absorbing and emitting power that the corresponding spectrum of absorption should be produced ; yet for a strong absorption to show itself, the hydrogen must be cool relatively to the source of radiation behind it, whether this be condensed particles or gas. Such con-ditions, it seems to me, should occur in the earlier rather than in the more advanced stages of condensation.

The subject is obscure, and we may go wrong in our mode of conceiving of the probable progress of events, but there can be no doubt that in one remarkable instance the white-star spectrum is associated with an early stage of condensation.

Sirius is one of the most conspicuous examples of one type of this class of stars. Photometric observations combined with its ascertained parallax show that this star emits from forty to sixty times the light of our sun, even to the eye, which is insensible to ultra-violet light, in which Sirius is very rich, while we learn from the motion of its companion that its mass is not much more than double that of our sun. It follows that, unless we attribute to this star an improbably great emissive power, it must be of immense size, and in a much more diffuse and therefore an earlier condition than our sun ; though probably at a later stage than those white stars in which the hydrogen lines are bright.

A direct determination of the relative temperature of the photospheres of the stars might possibly be obtained in some cases from the relative position of maximum radiation of their continuous spectra. Langley has shown that through the whole range of temperature on which we can experiment, and presumably at temperatures beyond, the maximum of radiation power in solid bodies gradually shifts upwards in the spectrum from the infra-red through the red and orange, and that in the sun it has reached the blue.

The defined character as a rule of the stellar lines of absorption suggests that the vapours producing them do not at the same time exert any strong power of general absorption. Consequently we should probably not go far wrong, when the photosphere consists of liquid or solid particles, if we could compare select parts of the con-tinuous spectrum between the stronger lines or where they are fewest. It is obvious that if extended portions of different stellar spectra were compared, their true relation would be obscured by the line-absorption.

The increase of temperature, as shown by the rise in the spectrum of the maximum of radiation, may not always be accompanied by a corresponding greater brightness of a star as estimated by the eye, which is an extremely imperfect photometric instrument. Not only is the eye blind to large regions of radiation, but even for the small range of light that we can see the visual effect varies enormously with its colour. According to Prof.

Langley, the same amount of energy which just enables us to perceive light in the crimson at A would in the green produce a visual effect 100,000 times greater. In the violet the proportional effect would be 1,600, in the blue 62,000, in the yellow 28,000, in the orange 14,000, and in the red 1,200. Captain Abney's recent experi-ments make the sensitiveness of the eye for the green near F to be 750 times greater than for red about C. It is for this reason, at least in part, that I suggested in 1864, and have since shown by direct observation, that the spectrum of the nebula in Andromeda, and pre-sumably of similar nebulæ, is in appearance only wanting in the red.

The stage at which the maximum radiation is in the green, corresponding to the eye's greatest sensitiveness, would be that in which it could be most favourably measured by eye-photometry. As the maximum rose into the violet and beyond, the star would increase in visual brightness, but not in proportion to the increase of energy radiated by it.

The brightness of a star would be affected by the nature of the substance by which the light was chiefly emitted. In the laboratory solid carbon exhibits the highest emis-sive power. A stellar stage in which radiation comes, to a large extent, from a photosphere of the solid particles of this substance, would be favourable for great brilliancy. Though the stars are built up of matter essentially similar to that of the sun, it does not follow that the proportion of the different elements is everywhere the same. It may be that the substances condensed in the photospheres of different stars may differ in their emissive powers, but probably not to a great extent.

All the heavenly bodies are seen by us through the tinted medium of our atmosphere. According to Langley, the solar stage of stars is not really yellow, but, even as gauged by our imperfect eyes, would appear bluish-white if we could free ourselves from the deceptive influences of our surroundings.

From these considerations it follows that we can scarcely infer the evolutional stages of the stars from a simple comparison of their eye-magnitudes. We should expect the white stars to be, as a class, less dense than the stars in the solar stage. As great mass might bring in the solar type of spectrum at a relatively earlier time, some of the brightest of these stars may be very massive and brighter than the sun—for example, the brilliant star Arcturus. For these reasons the solar stars should not only be denser than the white stars, but perhaps, as a class, surpass them in mass and eye-brightness.

It has been shown by Lane that, so long as a con-densing gaseous mass remains subject to the laws of a purely gaseous body, its temperature will continue to rise.

The greater or less breadth of the lines of absorption of hydrogen in the white stars may be due to variations of the depth of the hydrogen in the line of sight, arising from the causes which have been discussed. At the sides of the lines the absorption and emission are feebler than in the middle, and would come out more strongly with a greater thickness of gas.

The diversities among the white stars are nearly as numerous as the individuals of the class. Time does not permit me to do more than to record that, in addition to the three sub-classes into which they have been divided by Vogel, Scheiner has recently investigated minor differences as suggested by the character of the third line of hydrogen near G. He has pointed out, too, that so far as his observations go the white stars in the con-stellation of Orion stand alone, with the exception of Algol, in possessing a dark line in the blue which has apparently the same position as a bright line in the great nebula of the same constellation ; and Pickering finds, in his photographs of the spectra of these stars, dark lines corresponding to the principal lines of the bright-line stars, and the planetary nebulæ, with the exception of the chief nebular line. The association of white stars with nebular matter in Orion, in the Pleiades, in

the region of the Milky Way, and in other parts of the heavens, may be regarded as falling in with the view that I have taken.

In the stars possibly further removed from the white class than our sun, belonging to the first division of Vogel's third class, which are distinguished by absorption bands with their stronger edge towards the blue, the hydrogen lines are narrower than in the solar spectrum. In these stars the density gradient is probably still more rapid, the depth of hydrogen may be less, and possibly the hydrogen molecules may be affected by a larger number of encounters with dissimilar molecules. In some red stars with dark hydrocarbon bands the hydrogen lines have not been certainly observed; if they are really absent, it may be because the temperature has fallen below the point at which hydrogen can exert its characteristic absorption; besides, some hydrogen will have united with the carbon. The coming in of the hydrocarbon bands may indicate a later evolutional stage, but the temperature may still be high, as acetylene can exist in the electric arc.

A number of small stars, more or less similar to those which are known by the names of their discoverers, Wolf and Rayet, have been found by Pickering in his photographs. These are remarkable for several brilliant groups of bright lines, including frequently the hydrogen lines and the line D_3, upon a continuous spectrum strong in blue and violet rays, in which are also dark lines of absorption. As some of the bright groups appear in his photographs to agree in position with corresponding bright lines in the planetary nebulæ, Pickering suggests that these stars should be placed in one class with them, but the brightest nebular line is absent from these stars. The simplest conception of their nature would be that each star is surrounded by a nebula, the bright groups being due to the gaseous matter outside the star. Mr. Roberts, however, has not been able to bring out any indication of nebulosity by prolonged exposure. The remarkable star η Argus may belong to this class of the heavenly bodies.

In the nebulæ, the elder Herschel saw portions of the fiery mist or "shining fluid" out of which the heavens and the earth had been slowly fashioned. For a time this view of the nebulæ gave place to that which regarded them as external galaxies, cosmical "sandheaps," too remote to be resolved into separate stars; though indeed, in 1858, Mr. Herbert Spencer showed that the observations of nebulæ up to that time were really in favour of an evolutional progress.

In 1864 I brought the spectroscope to bear upon them; the bright lines which flashed upon the eye showed the source of the light to be glowing gas, and so restored these bodies to what is probably their true place, as an early stage of sidereal life.

At that early time our knowledge of stellar spectra was small. For this reason partly, and probably also under the undue influence of theological opinions then widely prevalent, I unwisely wrote in my original paper, in 1864, "that in these objects we no longer have to do with a special modification of our own type of sun, but find ourselves in presence of objects possessing a distinct and peculiar plan of structure." Two years later, however, in a lecture before this Association, I took a truer position. "Our views of the universe," I said, "are undergoing important changes; let us wait for more facts with minds unfettered by any dogmatic theory, and therefore free to receive the teaching, whatever it may be, of new observations."

Let us turn aside for a moment from the nebulæ in the sky to the conclusions to which philosophers had been irresistibly led by a consideration of the features of the solar system. We have before us in the sun and planets obviously not a haphazard aggregation of bodies, but a system resting upon a multitude of relations pointing to a common physical cause. From these considerations

Kant and Laplace formulated the nebular hypothesis, resting it on gravitation alone, for at that time the science of the conservation of energy was practically unknown. These philosophers showed how, on the supposition that the space now occupied by the solar system was once filled by a vaporous mass, the formation of the sun and planets could be reasonably accounted for.

By a totally different method of reasoning, modern science traces the solar system backward step by step to a similar state of things at the beginning. According to Helmholtz the sun's heat is maintained by the contraction of his mass, at the rate of about 220 feet a year. Whether at the present time the sun is getting hotter or colder we do not certainly know. We can reason back to the time when the sun was sufficiently expanded to fill the whole space occupied by the solar system, and was reduced to a great glowing nebula. Though man's life—the life of the race perhaps—is too short to give us direct evidence of any distinct stages of so august a process, still the probability is great that the nebular hypothesis, especially in the more precise form given to it by Roche, does represent broadly, notwithstanding some difficulties, the succession of events through which the sun and planets have passed.

The nebular hypothesis of Laplace requires a rotating mass of fluid which at successive epochs became unstable from excess of motion, and left behind rings, or more probably perhaps lumps, of matter from the equatorial regions.

The difficulties to which I have referred have suggested to some thinkers a different view of things, according to which it is not necessary to suppose that one part of the system gravitationally supports another. The whole may consist of a congeries of discrete bodies, even if these bodies be the ultimate molecules of matter. The planets may have been formed by the gradual accretion of such discrete bodies. On the view that the material of the condensing solar system consisted of separate particles or masses, we have no longer the fluid pressure which is an essential part of Laplace's theory. Faye, in his theory of evolution from meteorites, has to throw over this fundamental idea of the nebular hypothesis, and he formulates instead a different succession of events in which the outer planets were formed last—a theory which has difficulties of its own.

Professor George Darwin has recently shown, from an investigation of the mechanical conditions of a swarm of meteorites, that on certain assumptions a meteoric swarm might behave as a coarse gas, and in this way bring back the fluid pressure exercised by one part of the system on the other, which is required by Laplace's theory. One chief assumption consists in supposing that such inelastic bodies as meteoric stones might attain the effective elasticity of a high order which is necessary to the theory through the sudden volatilisation of a part of their mass at an encounter, by which what is virtually a violent explosive is introduced between the two colliding stones. Professor Darwin is careful to point out that it must necessarily be obscure as to how a small mass of solid matter can take up a very large amount of energy in a small fraction of a second.

Any direct indications from the heavens themselves, however slight, are of so great value that I should perhaps in this connection call attention to a recent remarkable photograph, by Mr. Roberts, of the great nebula in Andromeda. On this plate we seem to have presented to us some stage of cosmical evolution, on a gigantic scale. The photograph shows a sort of whirlpool disturbance of the luminous matter which is distributed in a plane inclined to the line of sight, in which a series of rings of bright matter separated by dark spaces, greatly foreshortened by perspective, surround a large undefined central mass. We are ignorant of the parallax of this nebula, but there can be little doubt that we are looking upon a system very remote, and therefore of a magnitude great beyond our power of adequate comprehension.

The matter of this nebula, in whatever state it may be, appears to be distributed, as in so many other nebulæ, in rings or spiral streams, and to suggest a stage in a succession of evolutional events not inconsistent with that which the nebular hypothesis requires. To liken this object more directly to any particular stage in the formation of the solar system would be "to compare things great with small," and might be indeed to introduce a false analogy; but, on the other hand, we should err through an excess of caution if we did not accept the remarkable features brought to light by this photograph as a presumptive indication of a progress of events in cosmical history following broadly upon the lines of Laplace's theory.

The old view of the original matter of the nebulæ, that it consisted of a "fiery mist,"—

> "a tumultuous cloud
> Instinct with fire and nitre,"

fell at once with the rise of the science of thermodynamics. In 1854 Helmholtz showed that the supposition of an original fiery condition of the nebulous stuff was unnecessary, since in the mutual gravitation of widely separated matter we have a store of potential energy sufficient to generate the high temperature of the sun and stars. We can scarcely go wrong in attributing the light of the nebulæ to the conversion of the gravitational energy of shrinkage into molecular motion.

The idea that the light of comets and of nebulæ may be due to a succession of ignited flashes of gas from the encounters of meteoric stones was suggested by Professor Tait, and was brought to the notice of this Association in 1871 by Sir William Thomson in his Presidential Address.

The spectrum of the bright-line nebulæ is certainly not such a spectrum as we should expect from the flashing by collisions of meteorites similar to those which have been analysed in our laboratories. The strongest lines of the substances which in the case of such meteorites would first show themselves — iron, sodium, magnesum, nickel, &c.—are not those which distinguish the nebular spectrum. On the contrary, this spectrum is chiefly remarkable for a few brilliant lines, very narrow and defined, upon a background of a faint continuous spectrum, which contains numerous bright lines, and probably some lines of absorption.

The two most conspicuous lines have not been interpreted; for though the second line falls near, it is not coincident with a strong double line of iron. It is hardly necessary to say that though the near position of the brightest line to the bright double line of nitrogen, as seen in a small spectroscope in 1864, naturally suggested at that early time the possibility of the presence of this element in the nebulæ, I have been careful to point out, to prevent misapprehension, that in more recent years the nitrogen line and subsequently a lead line have been employed by me solely as fiducial points of reference in the spectrum.

The third line we know to be the second line of the first spectrum of hydrogen. Mr. Keeler has seen the first hydrogen line in the red, and photographs show that this hydrogen spectrum is probably present in its complete form, or nearly so, as we first learnt to know it in the absorption spectrum of the white stars.

We are not surprised to find associated with it the line D_3, near the position of the absent sodium lines, probably due to the atom of some unknown gas, which in the sun can only show itself in the outbursts of highest temperature, and for this reason does not reveal itself by absorption in the solar spectrum.

It is not unreasonable to assume that the two brightest lines, which are of the same order, are produced by substances of a similar nature, in which a vibratory motion corresponding to a very high temperature is also necessary. These substances, as well as that represented by the line D_3, may be possibly some of the unknown elements which are wanting in our terrestrial chemistry between hydrogen and lithium, unless indeed D_3 be on the lighter side of hydrogen.

In the laboratory we must have recourse to the electric discharge to bring out the spectrum of hydrogen; but in a vacuum tube, though the radiation may be great, from the relative fewness of the luminous atoms or molecules, or from some other cause, the temperature of the gas as a whole may be low.

On account of the large extent of the nebulæ, a comparatively small number of luminous molecules or atoms would probably be sufficient to make the nebulæ as bright as they appear to us. On such an assumption the average temperature may be low, but the individual particles, which by their encounters are luminous, must have motions corresponding to a very high temperature, and in this sense be extremely hot.

In such diffuse masses, from the great mean length of free path, the encounters would be rare but correspondingly violent, and tend to bring about vibrations of comparatively short period, as appears to be the case if we may judge by the great relative brightness of the more refrangible lines of the nebular spectrum.

Such a view may perhaps reconcile the high temperature which the nebular spectrum undoubtedly suggests with the much lower mean temperature of the gaseous mass, which we should expect at so early a stage of condensation, unless we assume a very enormous mass; or that the matter coming together had previously considerable motion, or considerable molecular agitation.

The inquisitiveness of the human mind does not allow us to remain content with the interpretation of the present state of the cosmical masses, but suggests the question—

> "What see'st thou else
> In the dark backward and abysm of time?"

What was the original state of things? how has it come about that, by the side of ageing worlds, we have nebulæ in a relatively younger stage? Have any of them received their birth from dark suns, which have collided into new life, and so belong to a second or later generation of the heavenly bodies?

During the short historic period, indeed, there is no record of such an event; still it would seem to be only through the collision of dark suns, of which the number must be increasing, that a temporary rejuvenescence of the heavens is possible, and by such ebbings and flowings of stellar life that the inevitable end to which evolution in its apparently uncompensated progress is carrying us can, even for a little, be delayed.

We cannot refuse to admit as possible such an origin for nebulæ.

In considering, however, the formation of the existing nebulæ, we must bear in mind that, in the part of the heavens within our ken, the stars still in the early and middle stages of evolution exceed greatly in number those which appear to be in an advanced condition of condensation. Indeed we find some stars which may be regarded as not far advanced beyond the nebular condition.

It may be that the cosmical bodies which are still nebulous owe their later development to some conditions of the part of space where they occur, such as conceivably a greater original homogeneity, in consequence of which condensation began less early. In other parts of space condensation may have been still further delayed, or even have not yet begun. It is worthy of remark that these nebulæ group themselves about the Milky Way, where we find a preponderance of the white-star type of stars, and almost exclusively the bright-line stars which Pickering associates with the planetary nebulæ. Further, Dr. Gill concludes, from the rapidity with which they impress themselves upon the plate, that the fainter stars of the Milky Way also, to a large extent, belong to this early type of stars. At the same time other types of stars occur also over this region, and the red hydrocarbon stars are found in certain parts; but possibly these stars

may be before or behind the Milky Way, and not physically connected with it.

If light matter be suggested by the spectrum of these nebulæ, it may be asked further, as a pure speculation, whether in them we are witnessing possibly a later condensation of the light matter which had been left behind, at least in a relatively greater proportion, after the first growth of worlds into which the heavier matter condensed, though not without some entanglement of the lighter substances. The wide extent and great diffuseness of this bright-line nebulosity over a large part of the constellation of Orion may be regarded perhaps as pointing in this direction. The diffuse nebulous matter streaming round the Pleiades may possibly be another instance, though the character of its spectrum has not yet been ascertained.

In the planetary nebulæ, as a rule, there is a sensible increase of the faint continuous spectrum, as well as a slight thickening of the bright lines towards the centre of the nebula, appearances which are in favour of the view that these bodies are condensing gaseous masses.

Professor G. Darwin, in his investigation of the equilibrium of a rotating mass of fluid, found, in accordance with the independent researches of Poincaré, that when a portion of the central body becomes detached through increasing angular velocity, the portion should bear a far larger ratio to the remainder than is observed in the planets and satellites of the solar system, even taking into account heterogeneity from the condensation of the parent mass.

Now this state of things, in which the masses though not equal are of the same order, does seem to prevail in many nebulæ, and to have given birth to a large class of binary stars. Mr. See has recently investigated the evolution of bodies of this class, and points out their radical differences from the solar system in the relatively large mass-ratios of the component bodies, as well as in the high eccentricities of their orbits brought about by tidal friction, which would play a more important part in the evolution of such systems.

Considering the large number of these bodies, he suggests that the solar system should perhaps no longer be regarded as representing celestial evolution in its normal form—

> "A goodly Paterne to whose perfect mould
> He fashioned them" . . .

but rather as modified by conditions which are exceptional.

It may well be that, in the very early stages, condensing masses are subject to very different conditions, and that condensation may not always begin at one or two centres, but sometimes set in at a large number of points, and proceed in the different cases along very different lines of evolution.

Besides its more direct use in the chemical analysis of the heavenly bodies, the spectroscope has given to us a great and unexpected power of advance along the lines of the older astronomy. In the future a higher value may, indeed, be placed upon this indirect use of the spectroscope than upon its chemical revelations.

By no direct astronomical methods could motions of approach or of recession of the stars be even detected, much less could they be measured. A body coming directly towards us or going directly from us appears to stand still. In the case of the stars we can receive no assistance from change of size or of brightness. The stars show no true discs in our instruments, and the nearest of them is so far off that if it were approaching us at the rate of a hundred miles in a second of time, a whole century of such rapid approach would not do more than increase its brightness by the one-fortieth part.

Still it was only too clear that, so long as we were unable to ascertain directly those components of the stars' motions which lie in the line of sight, the speed and direction of the solar motion in space, and many of the great problems of the constitution of the heavens, must remain more or less imperfectly known. Now the spectroscope has placed in our hands this power, which, though so essential, appeared almost in the nature of things to lie for ever beyond our grasp; it enables us to measure directly, and under favourable circumstances to within a mile per second, or even less, the speed of approach or of recession of a heavenly body. This method of observation has the great advantage for the astronomer of being independent of the distance of the moving body, and is therefore as applicable and as certain in the case of a body on the extreme confines of the visible universe, so long as it is bright enough, as in the case of a neighbouring planet.

Doppler had suggested as far back as 1841 that the same principle, on which he had shown that a sound should become sharper or flatter if there were an approach or a recession between the ear and the source of the sound, would apply equally to light; and he went on to say that the difference of colour of some of the binary stars might be produced in this way by their motions. Doppler was right in that the principle is true in the case of light, but he was wrong in the particular conclusion which he drew from it. Even if we suppose a star to be moving with a sufficiently enormous velocity to alter sensibly its colour to the eye, no such change would actually be seen, for the reason that the store of invisible light beyond both limits of the visible spectrum, the blue and the red, would be drawn upon, and light-waves invisible to us would be exalted or degraded so as to take the place of those raised or lowered in the visible region, and the colour of the star would remain unchanged. About eight years later Fizeau pointed out the importance of considering the individual wave-lengths of which white light is composed. As soon, however, as we had learned to recognise the lines of known substances in the spectra of the heavenly bodies, Doppler's principle became applicable as the basis of a new and most fruitful method of investigation. The measurement of the small shift of the celestial lines from their true positions, as shown by the same lines in the spectrum of a terrestrial substance, gives to us the means of ascertaining directly in miles per second the speed of approach or of recession of the heavenly body from which the light has come.

An account of the first application of this method of research to the stars, which was made in my observatory in 1868, was given by Sir Gabriel Stokes from this chair, at the meeting at Exeter, in 1869. The stellar motions determined by me were shortly after confirmed by Prof. Vogel in the case of Sirius, and in case of other stars by Mr. Christie, now Astronomer Royal, at Greenwich; but, necessarily, in consequence of the inadequacy of the instruments then in use for so delicate an inquiry, the amounts of these motions were but approximate.

The method was shortly afterwards taken up systematically at Greenwich and at the Rugby Observatory. It is to be greatly regretted that, for some reasons, the results have not been sufficiently accordant and accurate for a research of such exceptional delicacy. On this account probably, as well as that the spectroscope at that early time had scarcely become a familiar instrument in the observatory, astronomers were slow in availing themselves of this new and remarkable power of investigation. That this comparative neglect of so truly wonderful a method of ascertaining what was otherwise outside our powers of observation, has greatly retarded the progress of astronomy during the last fifteen years, is but too clearly shown by the brilliant results which within the last couple of years have followed fast upon the recent masterly application of this method by photography at Potsdam, and by eye with the needful accuracy at the Lick Observatory. At last this use of the spectroscope has taken its true place as one of the most potent methods of astronomical research. It gives us the motions of approach and of recession, not in angular measures which depend for their translation into actual velocities upon

separate determinations of parallactic displacements, but at once in terrestrial units of distance.

This method of work will doubtless be very prominent in the astronomy of the near future, and to it probably we shall have to look for the more important discoveries in sidereal astronomy which will be made during the coming century.

In his recent application of photography to this method of determining celestial motions, Professor Vogel, assisted by Dr. Scheiner, considering the importance of obtaining the spectrum of as many stars as possible on an extended scale without an exposure inconveniently long, wisely determined to limit the part of the spectrum on the plate to the region for which the ordinary silver-bromide gelatine plates are most sensitive, namely, to a small distance on each side of G, and to employ as the line of comparison the hydrogen line near G, and recently also certain lines of iron. The most minute and complete mechanical arrangements were provided for the purpose of securing the absolute rigidity of the comparison spectrum relatively to that of the star, and for permitting temperature adjustments and other necessary ones to be made.

The perfection of these spectra is shown by the large number of lines, no fewer than 250 in the case of Capella, within the small region of the spectrum on the plate. Already the motions of about fifty stars have been measured with an accuracy, in the case of the larger number of them, of about an English mile per second.

At the Lick Observatory it has been shown that observations can be made directly by eye with an accuracy equally great. Mr. Keeler's brilliant success has followed in great measure from the use of the third and fourth spectra of a grating 14,438 lines to the inch. The marvellous accuracy attainable in his hands on a suitable star, is shown by observations on three nights of the star Arcturus, the largest divergence of his measures being not greater than six-tenths of a mile per second, while the mean of the three nights' work agreed with the mean of five photographic determinations of the same star at Potsdam to within one tenth of an English mile. These are determinations of the motions of a sun so stupendously remote that even the method of parallax practically fails to fathom the depth of intervening space, and by means of light-waves which have been, according to Elkin's nominal parallax, nearly 200 years upon their journey.

Mr. Keeler, with his magnificent means, has accomplished a task which I attempted in vain in 1874, with the comparatively poor appliances at my disposal, of measuring the motions in the line of sight of some of the planetary nebulæ. As the stars have considerable motions in space it was to be expected that nebulæ should possess similar motions, for the stellar motions must have belonged to the nebulæ out of which they have been evolved. My instrumental means, limiting my power of detection to motions greater than twenty-five miles per second, were insufficient. Mr. Keeler has found in the examination of ten nebulæ motions varying from two miles to twenty-seven miles, with one exceptional motion of nearly forty miles.

For the nebula of Orion Mr. Keeler finds a motion of recession of about ten miles a second. Now this motion agrees closely with what it should appear to have from the drift of the solar system itself, so far as it has been possible at present to ascertain the probable velocity of the sun in space. This grand nebula, of vast extent and of extreme tenuity, is probably more nearly at rest relatively to the stars of our system than any other celestial object we know; still, it would seem more likely than even here we have some motion, small though it may be, than that the motions of the matter of which it is formed were so absolutely balanced as to leave this nebula in the unique position of absolute immobility in the midst of whirling and drifting suns and systems of suns.

The spectroscopic method of determining celestial motions in the line of sight has recently become fruitful in a new but not altogether unforeseen direction, for it has, so to speak, given us a separating power far beyond that of any telescope the glass-maker and the optician could construct, and so enabled us to penetrate into mysteries hidden in stars apparently single, and altogether unsuspected of being binary systems. The spectroscope has not simply added to the list of the known binary stars, but has given to us for the first time a knowledge of a new class of stellar systems, in which the components are in some cases of nearly equal magnitude, and in close proximity, and are revolving with velocities greatly exceeding the planetary velocities of our system.

The K line in the photographs of Mizar, taken at the Harvard College Observatory, was found to be double at intervals of fifty-two days. The spectrum was therefore not due to a single source of light, but to the combined effect of two stars moving periodically in opposite directions in the line of sight. It is obvious that if two stars revolve round their common centre of gravity in a plane not perpendicular to the line of sight, all the lines in a spectrum common to the two stars will appear alternately single or double.

In the case of Mizar and the other stars to be mentioned, the spectroscopic observations are not as yet extended enough to furnish more than an approximate determination of the elements of their orbits.

Mizar especially, on account of its relatively long period, about 105 days, needs further observations. The two stars are moving each with a velocity of about fifty miles a second, probably in elliptical orbits, and are about 143 millions of miles apart. The stars of about equal brightness have together a mass about forty times as great as that of our sun.

A similar doubling of the lines showed itself in the Harvard photographs of β Aurigæ at the remarkably close interval of almost exactly two days, indicating a period of revolution of about four days. According to Vogel's later observations, each star has a velocity of nearly seventy miles a second, the distance between the stars being little more than seven and a half millions of miles, and the mass of the system 4·7 times that of the sun. The system is approaching us at the speed of about sixteen miles a second.

The telescope could never have revealed to us double stars of this order. In the case of β Aurigæ, combining Vogel's distance with Pritchard's recent determination of the star's parallax, the greatest angular separation of the stars as seen from the earth would be 1-200th part of a second of arc, and therefore very far too small for the highest powers of the largest telescopes. If we take the relation of aperture to separating power usually accepted, an object-glass of about eighty feet in diameter would be needed to resolve this binary star. The spectroscope, which takes no note of distance, magnifies, so to speak, this minute angular separation 4000 times; in other words, the doubling of the lines, which is the phenomenon that we have to observe, amounts to the easily measurable quantity of twenty seconds of arc.

There were known, indeed, variable stars of short period, which it had been suggested might be explained on the hypothesis of a dark body revolving about a bright sun in a few days, but this theory was met by the objection that no such systems of closely revolving suns were known to exist.

The Harvard photographs of which we have been speaking were taken with a slitless form of spectroscope, the prisms being placed, as originally by Fraunhofer, before the object-glass of the telescope. This method, though it possesses some advantages, has the serious drawback of not permitting a direct comparison of the star's spectrum with terrestrial spectra. It is obviously unsuited to a variable star like Algol, where one star only is bright, for in such a case there would be no doubling of the lines, but only a small shift to and fro of the lines of the bright star as it moved on its orbit alternately towards

and from our system, which would need for its detection the fiducial positions of terrestrial lines compared directly with them.

For such observations the Potsdam spectrograph was well adapted. Professor Vogel found that the bright star of Algol did pulsate backwards and forwards in the visual direction in a period corresponding to the known variation of its light. The explanation which had been suggested for the star's variability, that it was partially eclipsed at regular intervals of 68·8 hours by a dark companion large enough to cut off nearly five-sixths of its light, was therefore the true one. The dark companion, no longer able to hide itself by its obscureness, was brought out into the light of direct observation by means of its gravitational effects.

Seventeen hours before minimum Algol is receding at the rate of about 24½ miles a second, while seventeen hours after minimum it is found to be approaching with a speed of about 28½ miles. From these data, together with those of the variation of its light, Vogel found, on the assumption that both stars have the same density, that the companion, nearly as large as the sun, but with about one-fourth his mass, revolves with a velocity of about 55 miles a second. The bright star of about twice the size and mass moves about the common centre of gravity with the speed of about 26 miles a second. The system of the two stars, which are about 3¼ millions of miles apart, considered as a whole, is approaching us with a velocity of 2·4 miles a second. The great difference in luminosity of the two stars, not less than fifty times, suggests rather that they are in different stages of condensation, and dissimilar in density.

It is obvious that if the orbit of a star with an obscure companion is inclined to the line of sight, the companion will pass above or below the bright star and produce no variation of its light. Such systems may be numerous in the heavens. In Vogel's photographs, Spica, which is not variable, by a small shifting of its lines reveals a backward and forward periodical pulsation due to orbital motion. As the pair whirl round their common centre of gravity, the bright star is sometimes advancing, at others receding. They revolve in about four days, each star moving with a velocity of about 56 miles a second in an orbit probably nearly circular, and possess a combined mass of rather more than 2½ times that of the sun. Taking the most probable value for the star's parallax, the greatest angular separation of the stars would be far too small to be detected with the most powerful telescopes.

If in a close double star the fainter companion is of the white star type, while the bright star is solar in character, the composite spectrum would be solar with the hydrogen lines unusually strong. Such a spectrum would in itself afford some probability of a double origin, and suggest the existence of a companion star.

In the case of a true binary star the orbital motions of the pair would reveal themselves in a small periodical swaying of the hydrogen lines relatively to the solar ones.

Prof. Pickering considers that his photographs show ten stars with composite spectra; of these, five are known to be double. The others are—τ Persei, ζ Aurigæ, δ Sagittarii, 31 Ceti, and β Capricorni. Perhaps β Lyræ should be added to this list.

In his recent classical work on the rotation of the sun, Dunér has not only determined the solar rotation for the equator, but for different parallels of latitude up to 75°. The close accordance of his results shows that these observations are sufficiently accurate to be discussed with the variation of the solar rotation for different latitudes, which had been determined by the older astronomical methods from the observations of the solar spots.

Though I have already spoken incidentally of the invaluable aid which is furnished by photography in some of the applications of the spectroscope to the heavenly bodies, the new power which modern photography has put into the hands of the astronomer is so great, and has led already, within the last few years, to new acquisitions of knowledge of such vast importance, that it is fitting that a few sentences should be specially devoted to this subject.

Photography is no new discovery, being about half a century old; it may excite surprise, and indeed possibly suggest some apathy on the part of astronomers, that though the suggestion of the application of photography to the heavenly bodies dates from the memorable occasion when, in 1839, Arago, announcing to the Académie des Sciences the great discovery of Niepce and Daguerre, spoke of the possibility of taking pictures of the sun and moon by the new process, yet that it is only within a few years that notable advances in astronomical methods and discovery have been made by its aid.

The explanation is to be found in the comparative unsuitability of the earlier photographic methods for use in the observatory. In justice to the early workers in astronomical photography, among whom Bond, De la Rue, J. W. Draper, Rutherfurd, Gould, hold a foremost place, it is needful to state clearly that the recent great successes in astronomical photography are not due to greater skill, nor, to any great extent, to superior instruments, but to the very great advantages which the modern gelatine dry plate possesses for use in the observatory over the methods of Daguerre, and even over the wet collodion film on glass which, though a great advance on the silver plate, went but a little way towards putting into the hands of the astronomer a photographic surface adapted fully to his wants.

The modern silver-bromide gelatin plate, except for its grained texture, meets the needs of the astronomer at all points. It possesses extreme sensitiveness; it is always ready for use; it can be placed in any position; it can be exposed for hours; lastly, it does not need immediate development, and for this reason can be exposed again to the same object on succeeding nights, so as to make up by several instalments, as the weather may permit, the total time of exposure which is deemed necessary.

Without the assistance of photography, however greatly the resources of genius might overcome the optical and mechanical difficulties of constructing large telescopes, the astronomer would have to depend in the last resource upon his eye. Now we cannot by the force of continued looking bring into view an object too feebly luminous to be seen at the first and keenest moment of vision. But the feeblest light which falls upon the plate is not lost, but is taken in and stored up continuously. Each hour the plate gathers up 3600 times the light-energy which is received during the first second. It is by this power of accumulation that the photographic plate may be said to increase, almost without limit, though not in separating power, the optical means at the disposal of the astronomer for the discovery or the observation of faint objects.

Two principal directions may be pointed out in which photography is of great service to the astronomer. It enables him within the comparatively short time of a single exposure to secure permanently with great exactness the relative positions of hundreds or even of thousands of stars, or the minute features of nebulæ or other objects, or the phenomena of a passing eclipse, a task which by means of the eye and hand could only be accomplished, if done at all, after a very great expenditure of time and labour. Photography puts it in the power of the astronomer to accomplish in the short span of his own life, and so enter into their fruition, great works which otherwise must have been passed on by him as an heritage of labour to succeeding generations.

The second great service which photography renders is not simply an aid to the powers the astronomer already possesses. On the contrary, the plate, by recording light-waves which are both too small and too large to excite vision in the eye, brings him into a new region of knowledge, such as the infra-red and the ultra-violet parts of

the spectrum, which must have remained for ever unknown but for artificial help.

The present year will be memorable in astronomical history for the practical beginning of the Photographic Chart and Catalogue of the Heavens, which took their origin in an International Conference which met in Paris in 1887, by the invitation of M. l'Amiral Mouchez, Director of the Paris Observatory.

The richness in stars down to the ninth magnitude of the photographs of the comet of 1882 taken at the Cape Observatory under the superintendence of Dr. Gill, and the remarkable star charts of the Brothers Henry which followed two years later, astonished the astronomical world. The great excellence of these photographs, which was due mainly to the superiority of the gelatine plate, suggested to these astronomers a complete map of the sky, and a little later gave birth in the minds of the Paris astronomers to the grand enterprise of an International Chart of the Heavens. The actual beginning of the work this year is in no small degree due to the great energy and tact with which the Director of the Paris Observatory has conducted the initial steps, through the many delicate and difficult questions which have unavoidably presented themselves in an undertaking which depends upon the harmonious working in common of many nationalities, and of no fewer than eighteen observatories in all parts of the world. The three years since 1887 have not been too long for the detailed organisation of this work, which has called for several elaborate preliminary investigations on special points in which our knowledge was insufficient, and which have been ably carried out by Professors Vogel and Bakhuyzen, Dr. Trépied, Dr. Scheiner, Dr. Gill, the Astronomer Royal, and others. Time also was required for the construction of the new and special instruments.

The decisions of the Conference in their final form provide for the construction of a great photographic chart of the heavens with exposures corresponding to forty minutes' exposure at Paris, which it is expected will reach down to stars of about the fourteenth magnitude. As each plate is to be limited to four square degrees, and as each star, to avoid possible errors, is to appear on two plates, over 22,000 photographs will be required. For the more accurate determination of the positions of the stars, a *réseau* with lines at distances of 5 m.m. apart is to be previously impressed by a faint line upon the plate, so that the image of the *réseau* will appear together with the images of the stars when the plate is developed. This great work will be divided, according to their latitudes, among eighteen observatories provided with similar instruments, though not necessarily constructed by the same maker. Those in the British dominions and at Tacubaya have been constructed by Sir Howard Grubb.

Besides the plates to form the great chart, a second set of plates for a catalogue is to be taken, with a shorter exposure, which will give stars to the eleventh magnitude only. These plates, by a recent decision of the Permanent Committee, are to be pushed on as actively as possible, though, as far as may be practicable, plates for the chart are to be taken concurrently. Photographing the plates for the catalogue is but the first step in this work, and only supplies the data for the elaborate measurements which have to be made, which are, however, less laborious than would be required for a similar catalogue without the aid of photography.

Already Dr. Gill has nearly brought to conclusion, with the assistance of Professor Kapteyn, a preliminary photographic survey of the Southern heavens.

With an exposure sufficiently long for the faintest stars to impress themselves upon the plate, the accumulating action still goes on for the brighter stars, producing a great enlargement of their images from optical and photographic causes. The question has occupied the attention of many astronomers, whether it is possible to find a law connecting the diameters of these more or less over-

exposed images with the relative brightness of the stars themselves. The answer will come out undoubtedly in the affirmative, though at present the empirical formulæ which have been suggested for this purpose differ from each other. Captain Abney proposes to measure the total photographic action, including density as well as size, by the obstruction which the stellar image offers to light.

A further question follows as to the relation which the photographic magnitudes of stars bear to those determined by eye. Visual magnitudes are the physiological expression of the eye's integration of that part of the star's light which extends from the red to the blue. Photographic magnitudes represent the plate's integration of another part of the star's light, namely, from a little below where the power of the eye leaves off in the blue, to where the light is cut off by the glass, or is greatly reduced by want of proper corrections when a refracting telescope is used. It is obvious that the two records are taken by different methods in dissimilar units of different parts of the star's light. In the case of certain coloured stars the photographic brightness is very different from the visual brightness; but in all star changes, especially of a temporary character, may occur in the photographic or the visual region, unaccompanied by a similar change in the other part of the spectrum. For these reasons it would seem desirable that the two sets of magnitudes should be tabulated independently, and be regarded as supplementary of each other.

The determination of the distances of the fixed stars from the small apparent shift of their positions when viewed from widely separated positions of the earth in its orbit, is one of the most refined operations of the observatory. The great precision with which this minute angular quantity, a fraction of a second only, has to be measured, is so delicate an operation with the ordinary micrometer, though, indeed, it was with this instrument that the classical observations of Sir Robert Ball were made, that a special instrument, in which the measures are made by moving the two halves of a divided object-glass, known as a heliometer, has been pressed into this service, and quite recently, in the skilful hands of Dr. Gill and Dr. Elkin, has largely increased our knowledge in this direction.

It is obvious that photography might be here of great service, if we could rely upon measurements of photographs of the same stars taken at suitable intervals of time. Professor Pritchard, to whom is due the honour of having opened this new path, aided by his assistants, has proved by elaborate investigations that measures for parallax may be safely made upon photographic plates, with, of course, the advantages of leisure and repetition; and he has already by this method determined the parallax for twenty-one stars with an accuracy not inferior to that of values previously obtained by purely astronomical methods.

The remarkable successes of astronomical photography, which depend upon the plate's power of accumulation of a very feeble light acting continuously through an exposure of several hours, are worthy to be regarded as a new revelation. The first chapter opened when, in 1880, Dr. Henry Draper obtained a picture of the nebula of Orion; but a more important advance was made in 1883, when Dr. Common, by his photographs, brought to our knowledge details and extensions of this nebula hitherto unknown. A further disclosure took place in 1885, when the Brothers Henry showed for the first time in great detail the spiral nebulosity issuing from the bright star Maia of the Pleiades, and shortly afterwards nebulous streams about the other stars of this group. In 1886 Mr. Roberts, by means of a photograph to which three hours' exposure had been given, showed the whole background of this group to be nebulous. In the following year Mr. Roberts more than doubled for us the great extension of the nebular region which surrounds the trapezium in the constellation of Orion. By his photographs of the great

nebula in Andromeda, he has shown the true significance of the dark canals which had been seen by the eye. They are in reality spaces between successive rings of bright matter, which appeared nearly straight owing to the inclination in which they lie relatively to us. These bright rings surround an undefined central luminous mass. I have already spoken of this photograph.

Some recent photographs by Mr. Russell show that the great rift in the Milky Way in Argus, which to the eye is void of stars, is in reality uniformly covered with them. Also quite recently Mr. George Hale has photographed the prominences by means of a grating, making use of the lines H and K.

The heavens are richly but very irregularly inwrought with stars. The brighter stars cluster into well-known groups upon a background formed of an enlacement of streams and convoluted windings and intertwined spirals of fainter stars, which becomes richer and more intricate in the irregularly rifted zone of the Milky Way.

We, who form part of the emblazonry, can only see the design distorted and confused; here crowded, there scattered, at another place superposed. The groupings due to our position are mixed up with those which are real.

Can we suppose that each luminous point has no relation to the others near it than the accidental neighbourship of grains of sand upon the shore, or of particles of the wind-blown dust of the desert? Surely every star from Sirius and Vega down to each grain of the light-dust of the Milky Way has its present place in the heavenly pattern from the slow evolving of its past. We see a system of systems, for the broad features of clusters and streams and spiral windings which mark the general design are reproduced in every part. The whole is in motion, each point shifting its position by miles every second, though from the august magnitude of their distances from us and from each other, it is only by the accumulated movements of years or of generations that some small changes of relative position reveal themselves.

The deciphering of this wonderfully intricate constitution of the heavens will be undoubtedly one of the chief astronomical works of the coming century. The primary task of the sun's motion in space together with the motions of the brighter stars has been already put well within our reach by the spectroscopic method of the measurement of star-motions in the line of sight.

From other directions information is accumulating: from photographs of clusters and parts of the Milky Way, by Roberts in this country, Barnard at the Lick Observatory, and Russell at Sydney; from the counting of stars, and the detection of their configurations, by Holden and by Backhouse; from the mapping of the Milky Way by eye, at Parsonstown; from photographs of the spectra of stars, by Pickering at Harvard and in Peru; and from the exact portraiture of the heavens in the great international star chart which begins this year.

I have but touched some only of the problems of the newer side of astronomy. There are many others which would claim our attention if time permitted. The researches of the Earl of Rosse on lunar radiation, and the work on the same subject and on the sun, by Langley. Observations of lunar heat with an instrument of his own invention by Mr. Boys; and observations of the variation of the moon's heat with its phase by Mr. Frank Very. The discovery of the ultra-violet part of the hydrogen spectrum, not in the laboratory, but from the stars. The confirmation of this spectrum by terrestrial hydrogen in part by H. W. Vogel, and in its all but complete form by Cornu, who found similar series in the ultra-violet spectra of aluminium and thallium. The discovery of a simple formula for the hydrogen series by Balmer. The important question as to the numerical spectral relationship of different substances, especially in connection with their chemical properties; and the further question as to the origin of the harmonic and other relations between the lines and the groupings of lines of spectra; on these points contributions during the past year have been made by Rudolf v. Kövesligethy, Ames, Hartley, Deslandres, Rydberg, Grünwald, Kayser and Runge, Johnstone Stoney, and others. The remarkable employment of interference phenomena by Professor Michelson for the determination of the size, and distribution of light within them, of the images of objects which when viewed in a telescope subtend an angle less than that subtended by the light-wave at a distance equal to the diameter of the objective. A method applicable not alone to celestial objects, but also to spectral lines, and other questions of molecular physics.

Along the older lines there has not been less activity; by newer methods, by the aid of larger or more accurately constructed instruments, by greater refinement of analysis, knowledge has been increased, especially in precision and minute exactness.

Astronomy, the oldest of the sciences, has more than renewed her youth. At no time in the past has she been so bright with unbounded aspirations and hopes. Never were her temples so numerous, nor the crowd of her votaries so great. The British Astronomical Association formed within the year numbers already about 600 members. Happy is the lot of those who are still on the eastern side of life's meridian!

Already, alas! the original founders of the newer methods are falling out—Kirchhoff, Ångström, D'Arrest, Secchi, Draper, Becquerel; but their places are more than filled; the pace of the race is gaining, but the goal is not and never will be in sight.

Since the time of Newton our knowledge of the phenomena of Nature has wonderfully increased, but man asks, perhaps more earnestly now than in his days, what is the ultimate reality behind the reality of the perceptions? Are they only the pebbles of the beach with which we have been playing? Does not the ocean of ultimate reality and truth lie beyond?

CONTRIBUTIONS TO THE CHEMISTRY OF ERBIUM AND DIDYMIUM.*

By GERHARD KRÜSS.

(Continued from p. 76).

THIS value is not remote from the atomic weight of yttrium, and it is natural that yttria, as a powerful base, should follow didymia. The value found, rather higher than $Y = 90$, will have been produced by a slight admixture of terbia, since the oxide obtained by the ignition of the oxalates was yellowish, and not white, like yttria. It is also more probable that terbia, the more powerful base, should follow didymia on fractionation with ammonia than the feebly basic ytterbia.

The double sulphates precipitated by potassium sulphate were converted into nitrate, and the treatment of the didymium with a very large excess of potassium sulphate was again repeated, when only very small quantities of yttria were obtained. The yttria had therefore been almost entirely removed from the didymia by the former treatment.

Whilst potassium-didymium sulphate is very sparingly soluble, the potassium-yttrium sulphate dissolves in 7—8 parts of a slightly acid solution of potassium sulphate.

In order to remove from the didymium any lanthanum possibly present, the precipitated double sulphates were dissolved in much water, precipitated with ammonia, and dissolved in sulphuric acid after washing the potassium salt out of the precipitate. The sulphate obtained was

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* *Liebig's Annalen.*

evaporated, converted into the anhydrous salt, and added to ice-water in small portions with constant stirring. The sulphate dissolved slowly but completely, and was heated to 40° according to Mosander's method, and afterwards to a higher temperature. No separation of lanthanum sulphate took place, and the sulphate which remained in solution was again converted into nitrate. In this manner there was obtained from gadolinite a pure preparation of didymium. It contained mere traces of samarium; scandium could scarcely be present at the outset, as the crude earths had been most carefully fractionated with ammonia, and scandium would be more likely to accompany erbium than didymium.

The requisites were—

1. A relatively short series of fractional precipitations with ammonia, from a very dilute solution (removal of cerium, ytterbium, scandium, erbium).

2. Treatment with chlorine in an alkaline liquid (removal of the last traces of cerium).

3. Twice crystallisation with an excess of potassium sulphate (removal of yttrium and terbium).

4. Heating the solution of anhydrous sulphate in ice-water to 40° (removal of lanthanum).

Instead of often repeating this last method in case of a large quantity of lanthanum, it is better to precipitate fractionally with ammonia, as proposed by Cleve, when lanthanum behaves as the more powerful base.

The didymium obtained had a mean atomic weight of $\overset{\text{III}}{R} = 145$, and its preparation was relatively convenient. Erbium material could also be obtained from the above mentioned more feebly basic ammonia fractions of the earths gadolinite, without a fractionated decomposition of the nitrates by heat.

Fractionation of Erbium Material by Aniline in an Alcoholic Solution.

Erbia can be naturally more easily separated by fractionated precipitation from the stronger bases of the rare earths, such as didymia, than from the other weak bases, the oxides of holmium, thulium, and ytterbium. An approximate separation of these earths,—at least, as far as the preparation of pure ytterbium is concerned—may certainly be effected by resolving the mixed earthy nitrates by cautious fusion partially into basic salts insoluble in water, and repeating this fractionation systematically about 500 times. (See Nilson's "Researches on Ytterbium and Scandium," *Berichte Deutsch. Chem. Gesell.*, xiii., 1430, 1439; xii., 550, 554).

It was not practicable to separate quickly the feebly basic rare earths from each other by fractionated precipitation with ammonia. The author further tried whether a method for separating erbium from holmium, thulium, and ytterbium might be found upon Lecoq de Boisbaudran's observation (*Comptes Reudus*, cxi., 394), that the rare earths in presence of ammonium acetate are slowly and only partially precipitable by an excess of ammonia. The results were negative.

The following experiments were successful:—

On fractionating the earths with ammonia all the weak bases were accumulated in the fractions rich in erbium. The rare earths which accompany erbia, and erbia itself, under the experimental conditions above described, had behaved as bases weaker than ammonia diluted as above. A weaker base than dilute ammonia had therefore to be used if a precipitant was sought for separating, *e.g.*, erbia from ytterbia. It must be more strongly basic than ytterbia, but weaker than erbia, and consequently it must either not precipitate erbia at all from its solutions, or but very imperfectly.

Attempts were made to precipitate alcoholic solutions of neutral earthy salts, with alcoholic solutions of substituted ammonias. For this purpose the chlorides of the rare earths were used, the solutions being purified as far as possible from free hydrochloric acid by repeated evaporation upon the water bath. The purpose of this elimination of acid was to prevent the excess of hydrochloric acid from forming at once with aniline a hydrochlorate, which, if present in considerable quantities, greatly interferes with the precipitation even of the weakest bases among the rare earths by aniline.

The chlorides were taken up in alcohol at 50 per cent, and the organic bases were also dissolved in alcohol of the same strength.

If an earthy chloride which contains all the earths of gadolinite is first mixed with more aniline than is calculated according to the mean equivalent weight of the oxides, on the supposition that all oxide is precipitated, it appears, in fact, that the solution of chloride is only partially precipitated as hydroxide. If the solution containing an excess of aniline is filtered off and heated for some time to about 80°, there occurs a new precipitation of hydroxide, and even still a part of the earthy chloride is not decomposed by the excess of aniline present.

Aniline has thus behaved as a base feebler than a part of the rare earths. At the same time it is perceived that the aniline precipitations at the temperature of the room possess a fainter absorption spectrum than the precipitations at higher temperatures, the conditions being otherwise equal. At lower temperatures relatively more colourless earths are precipitated, and as these were first separated out of the mixture they were the weakest earths, especially therefore ytterbia.

Consequently aniline seemed suitable to eliminate the weakest bases from a material rich in erbia. In order to bring into more prominence the different behaviour of aniline in heat and cold, alcoholic solutions of chlorides of erbium material were mixed at 0° with an excess of alcoholic solutions of aniline. No precipitation took place, whence they were gradually heated by standing in the room until precipitation began. The liquid was then filtered, and the atomic weights of the earthy metals in the solution and the precipitate were determined.

Experiment 1.—A solution of chloride, containing chiefly erbium and ytterbium and some yttrium, was resolved under the conditions given into an aniline precipitate and a filtrate. The earthy mixture used in the experiment when converted from oxide into sulphate $\overset{\text{III}}{R}$ had the weight $= 161\cdot81$. The determination of the equivalents of the oxides present in the filtrate, and in the aniline precipitate, gave for the precipitate $\overset{\text{III}}{R} = 168\cdot75$, and for the filtrate $\overset{\text{III}}{R} = 158\cdot38$.

Experiment 2 was conducted under the same conditions with a material which contained in addition to erbium and ytterbium relatively much yttrium.

	Atom Weight.
$\overset{\text{III}}{R}$ in the earth employed..	$=131\cdot07$
„ „ oxide of the aniline precipitate ..	$=151\cdot13$
„ „ „ „ filtrate..	$=128\cdot92$

The precipitation of the earthy hydroxides with an alcoholic solution of aniline in the cold is an easy and neat operation, and if executed *only once* resolves an erbium material containing oxides of closely approximating basicity to a very considerable degree, as the above figures show.

Hence, large quantities of materials rich in erbium should be systematically worked up by precipitation with aniline, and the behaviour of "old" erbium should be tested by fractionated treatment with other ammonia bases.

Behaviour of the Earths with Ammonium Carbonate.

We learn from the researches of Berzelius, H. Rose, Marignac, Höglund, Stapff, that salts of lanthanum, yttrium, erbium, glucinum, thorium, and zirconium are precipitated by ammonium carbonate, and that the precipitated basic carbonates are re-dissolved in part readily and in part gradually in an excess of ammonium carbonate. Basic didymium carbonate, however, according to

Marignac, is almost insoluble in an excess of ammonium carbonate.

A neutral nitric solution of mixed earths of gadolinite was poured, whilst stirring, into a concentrated solution of ammonium carbonate (10 parts carbonate to 1 part of earth), and the precipitate was digested for 24 hours in the supernatant liquid. After the precipitate had been washed upon the filter with a solution of ammonium carbonate it was converted into nitrate. In its spectrum didymium lines were almost exclusively visible, and the erbium lines had nearly disappeared. If the material was rich in erbium the digestion with carbonate must be frequently repeated.

A current of steam is then passed through the mixed filtrates for some hours, when the ammonium carbonate is decomposed and a basic carbonate is deposited. This was filtered and converted into neutral nitrate. In its spectrum few didymium lines are present, but almost exclusively erbium and X lines. According to its spectrum the erbium, after being once digested, is almost as pure as if it had been obtained from a mixture of erbium and didymium by a twice repeated treatment of the mixed saline solution with potassium sulphate.

It must be remarked that erbium carbonate is but slightly soluble in ammonium carbonate, especially when, as in the case before us, it has been precipitated as a basic carbonate along with didymium. Thus, in the above experiment, from about 400 grms. of mixed earths, certainly poor in erbia, there were obtained only 5 grms. of erbia by a single digestion with ammonium carbonate. The above method is not adapted for obtaining large quantities of erbia from a mixture of the earths which yield absorption spectra; for this purpose fractionation with ammonia is preferable. But it is advantageous to digest didymium containing only small quantities of erbium with an excess of ammonium carbonate.

(To be continued.)

NOTICES OF BOOKS.

The International Annual of Anthony's Photographic Bulletin. New York : E. and H. T. Anthony and Co. London : Iliffe and Son.

THIS publication, now in its fourth year, consists of a selection of essays relative to the practical or to the theoretical phase of photography. These chapters are necessarily of a very promiscuous character. A humorous essay " To Correspondents " touches on the difficulties of an editor required by his readers to be omniscient. Says the writer :—" Time was when questions anent the sciences, the fine arts, and the industrial arts, were propounded by those in search of useful knowledge in various technical journals ; but with the advent of the ' press the button ' system we have reached the present stage in the process of levelling, and Susan Jane can study in the pages of her especial organ, the *Family Journal*, how to remove superfluous hair from the female face, how to repel the advances of a too forward milkman, and what is the best developer for dry plates, which, no matter how long a time or how short a time they are exposed, never have any picture upon them when finished."

On the applications of photography in scientific research we find but little. Still there is, we think, evidence here, as elsewhere, that photographers are now less exclusively given to taking portraits than was the case in the infancy of the art. The conflict between the amateur and the professional, and, again, the controversy between photography and " high art," are still raging.

One of the writers mentions, incidentally, that the present rage for photography has superseded the microscopy-fever of the last decennium. The selfsame hands that then manipulated the microscope and its accessories now wield the camera. Unfortunately a majority do as little good with one instrument as with the other.

The Chemical Analysis of Iron. A Complete Account of all the best known Methods for the Analysis of Iron, Steel, Pig-iron, Iron-ore, Limestone, Slag, Clay, Sand, Coal, Coke, and Furnace and Produce Gases. By ANDREW ALEXANDER BLAIR. Second Edition, 8vo., pp. 314. Philadelphia : J. B. Lippincott and Co.

WE are not surprised that a second edition of this useful and trustworthy work has been already called for. In general arrangement the present edition differs little from its forerunner, but a variety of modifications have been introduced in accordance with recent improvements in chemical analysis.

The get-up of the book has a much more ornamental character than we usually find among scientific publications. The illustrations are beautifully clear. Marginal notes furnish a running key to the subject-matter of the text, and will save the reader much trouble. At the same time footnotes give the authors of the various methods. The paper is of that glazed or calendered quality which has now become so fashionable, but which we think is not to be recommended, as the light which it reflects is fatiguing to the eyes.

CORRESPONDENCE.

THE INSTITUTE AND THE ALIEN.

To the Editor of the Chemical News.

SIR,—A great scandal has come to light among public analysts. The provisions of the Alien Act render aliens ineligible for the office of public analyst. The Local Government Board, which has to confirm each appointment of a public analyst before he can enter upon the discharge of the duties of his office, would not knowingly sanction the appointment of aliens, and yet, notwithstanding the Act and the Board, it is undeniable that for years several of these appointments have been in alien hands. The matter is grave,—far graver than would appear at first sight.

There is no doubt whatever of the state of the law in this respect, and the alien public analyst is no public analyst at all, but a mere counterfeit of the duly qualified public officer. Every tradesman who has been convicted and punished, in cases where the services of the alien public analyst have been required, is entitled to demand the quashing of the proceedings in his case on the score of flagrant irregularity.

The existence of such a being as the alien public analyst was made out a short time ago by my friend Mr. Johnstone, who took the bold step of writing to the authorities in districts where the public analyst was an alien, and offering himself as a candidate for the vacant office. The alien who has been usurping the office of public analyst for many years, and has thereby created a great scandal, complained to the Institute of Chemistry, which forthwith expelled Mr. Johnstone, who has performed a signal public service, they mistaking that performance for unprofessional conduct.—I am, &c.,

J. ALFRED WANKLYN.

MISCELLANEOUS.

Honours for Scientific Men.—*A propos* of the fact that Dr. Hyde Mijake, Professor in the Medical Faculty of the University of Tokio, has been nominated a member of the Japanese House of Peers, a medical contem-

porary complains that "in our highly favoured country" medical men, however eminent, can rise no higher than to a baronetcy. With scientific men in general the case is the same. We have had among us a family, two members of which—father and son—achieved a world wide and an enduring reputation for scientific researches. A baronetcy was awarded to them ; but the grandson, throwing himself into law and politics, has gained a peerage, though his celebrity is small indeed compared to that of his father and grandfather. Leaving law and finance out of the question, even literature has scored four peerages within the lifetime of the present generation, — Science none ! Would not a large proportion of our best minds be attracted to Science if it was not, in the distribution of honours, so entirely left out in the cold ?

New Decree concerning Methylated Spirit. — In addition to the 10 per cent of (impure) methylic alcohol with which alcohol has to be spoiled, in this country, before it can be sold duty-free for industrial purposes, the Board of Inland Revenue now demand that there shall be further added, in every 100 gallons, 12 gills of mineral naphtha of the specific gravity of not less than 0·800. We fear that this addition will interfere with some of the technical uses of this spirit. Why do not the advisers of the Inland Revenue recommend the addition of a trace of Dippel's animal oil, which renders the mixture absolutely undrinkable, whilst, from the minuteness of the dose required, it does not perplex the manufacturer ?

Gautter's Method for the Determination of Tannin. —MM. Schroeder and Passler.—The authors criticise Gautter's method, which they consider one of the best of the known processes. It has an advantage over that of Löwenthal, as it can be carried out without extensive previous experience and gives concordant results. On the other hand, Löwenthal's method has the advantage that substances other than tannin, such as hydrocarbons and organic acids, are not acted upon. Gautter's method is not applicable for determining the tannin in dye liquors. The authors operate as follows :—The liquid to be titrated is placed in a flask holding 350 c.c., and heated to a gentle boil after the addition of 0·5 c.c. dilute sul-phuric acid (1 : 5) to 1 m.grm. of the dry tannin substance. The flask is then removed from the fire, the solution of permanganate is let flow in by 1 c.c. at a time, shaking for five seconds after each addition. The red colour dis-appears more and more slowly, and ultimately remains after shaking for five seconds. The contents of the flask are then again heated to boiling, permanganate is again run in by c.c.'s, keeping the liquid boiling for one minute after each addition. This addition is continued until there is formed a copious precipitate of manganese hydroxide, which scarcely decreases after boiling for a minute. The number of c.c. consumed is noted, and the titration is considered satisfactory only if the solution consumed comes to 1—2 c.c. more than the final result shows. After the appearance of the strong permanent precipitate 5 c.c. permanganate are further added without heating; oxalic acid is then added until the solution be-comes perfectly clear, and it is then titrated to completion with permanganate. At the end of the titration they take the point when the red colour remains for half a minute. For standardising the authors use a solution of tannin containing about 2 grms. dry substance per litre, using from 10—25 c.c. of this solution for titration. In disputed cases the gravimetric method must be regarded as decisive.—*Zeit. für Anal. Chemie*, xxix., Part 6.

Purification of Sulphuretted Hydrogen for Criminal Investigations. — Oscar Jacobson (*Berichte*).—Arsenic hydride and iodine decompose each other to arsenic iodide and hydriodic acid, whilst hydrogen sulphide has no action upon iodine, either solid or dissolved, in strong hydriodic acid. Sulphuretted hydrogen can be obtained absolutely free from arsenic if passed over solid iodine.— *Zeit. für Anal. Chemie*, xxix., Part 6.

THE CHEMICAL NEWS.

ADDRESS TO THE CHEMICAL SECTION

OF THE

BRITISH ASSOCIATION.

By Professor W. C. ROBERTS-AUSTEN, C.B., F.R.S.,
President of the Section.

CARDIFF, 1891.

THE selection of Cardiff as a place of meeting of the British Association led to the presidency of Section B being entrusted to a metallurgist. It will be well, therefore, to deal in this address mainly with considerations connected with the subject to which my life has been devoted, and I hope that it may be possible for me to show that this practical art has both promoted the advancement of science and has received splendid gifts in return.

It is an art for which in this country we have traditional love; nevertheless the mode of teaching it, and its influence on science, are but imperfectly understood and appreciated. Practical metallurgists are far too apt to think that improvements in their processes are mainly the result of their own experience and observation, unaided by pure science. On the other hand, those who teach metallurgy often forget that for the present they have not only to give instruction in the method of conducting technical operations, but have truly to educate, by teaching the chemistry of high temperatures, at which ordinary reactions are modified or even reversed, while they have further to deal with many phenomena of much importance, which cannot, as yet, be traced to the action of elements in fixed atomic proportions, or in which the direct influence of the atom is only beginning to be recognised.

The development of a particular art, like that of an organism, proceeds from its internal activity; it is work which promotes its growth and not the external influence of the environment. In the early stage of the development of an industry the craftsmen gather a store of facts which afford a basis for the labours of the investigator, who penetrates the circle of the "mystery" and renders knowledge scientific. Browning, inspired by the labours of a chemist, finely tells us in his "Paracelsus":—

> To know
> Rather consists in opening out a way
> Whence the imprisoned splendor may escape,
> Than in effecting entry for a light
> Supposed to be without.

If it be asked who did most in gaining the industrial treasure and in revealing the light of chemical knowledge, the answer is certainly the metallurgists whose labours in this respect differ materially from others which have ministered to the welfare of mankind. First it may be urged that in no other art have the relations between theory and practice been so close and enduring. Bacon, who never undervalued research, tells us that in the division of the labour of investigation in the New Atlantis there are some "that raise the former discoveries by experiment into greater observations, axioms, and aphorisms: these we call the *interpreters of nature.*" There are also others "that bend themselves, looking into the experiments of their fellows and casting about how to draw out of them things of use and practice for man's life and knowledge . . . these we call the *dowry men or benefactors.*" In reviewing the history of metallurgy, especially in our islands, it would seem that the two classes of workers, the interpreters of nature and the practical men, have for centuries sat in joint committee,

and, by bringing theoretical speculation into close connection with hard industrial facts, have "carried us nearer the essence of truth."

The main theme of this address will therefore be the relation between theory and practice in metallurgy, with special reference to the indebtedness of the practical man to the scientific investigator.

We will then consider—

(1). Certain facts connected with "Oxidation" and "Reduction," upon which depend operations of special importance to the metallurgist.

(2). The influence in metallurgical practice of reactions which are either limited or reversible.

(3). The means by which progress in the metallurgic art may be effected, and the special need for studying the molecular constitution of metals and alloys.

(1). The present year is a memorable one for chemists, being the centenary of the birth of Faraday and the bi-centenary of the death of Robert Boyle. The work of the former has recently been lovingly and fittingly dealt with in the Royal Institution, where he laboured so long. I would, in turn, briefly recal the services of Boyle, not, however, on account of the coincidence of date, but because with him a new era in chemistry began. He knew too much about the marvellous action of "traces" of elements on masses of metal to feel justified in pronouncing absolutely against the possibilities of transmutation, but he did splendid service by sweeping away the firm belief that metals consist of sulphur, salt, and mercury, and by giving us the definition of an element. He recognised the preponderating influence of metallurgy in the early history of science, and quaintly tells us that "those addicted to chemistry have scarce any views but to the preparation of medicines or to the improvement of metals," a statement which was perfectly correct, for chemistry was built up on a therapeutic as well as a metallurgic basis. The fact is, however, that neither the preparation of materials to be employed in healing, nor the study of their action, had anything like the influence on the growth of theoretical chemistry which was exerted by a few simple metallurgical processes. Again, strange as it may seem, theoretical chemistry was more directly advanced by observations made in connection with methods of purifying the precious metals, and by the recognition of the quantitative significance of the results, than by the acquisition of facts incidentally gathered in the search for a transmuting agent. The belief that chemistry "grew out of alchemy" nevertheless prevails, and has found expression in this Section of the British Association. As a fact, however, the great metallurgists treated the search for a transmuting agent with contempt, and taught the necessity of investigation for its own sake. George Agricola, the most distinguished of the sixteenth-century metallurgists, in his work "De Ortu et Causis Subterraneorum" (lib. v.), written about the year 1539, disdainfully rejects both the view of the alchemists that metals consist of sulphur and mercury, and their pretended ability to change silver into gold by the addition of foreign matter.

Biringuccio (1540) says:—"I am one of those who ignore the art of the alchemists entirely. They mock nature when they say that with their medicines they correct its defects, and render imperfect metals perfect." "The art," he adds, "was not worthy of the consideration of the wise ancients who strove to obtain possible things." In his time, reaction between elements meant their destruction and re-constitution, nevertheless his sentence "transmutation is impossible, because in order to transmute a body you must begin by destroying it altogether," suggests that he realised the great principle of the conservation of mass upon which the science of chemistry is based. We have also the testimony of the German metallurgist, Becher, who improved our tin-smelting in Cornwall. He is said to have caused a medal

to be struck in 1675, which bore the legend: " Hanc unciam argenti finissimi ex plumbo arte alchymica transmutavi," though he should have been aware that he had only extracted the precious metal from the lead, and had not transmuted the base one. This is a lapse which must be forgiven him, for his *terra pinguis* was the basis of the theory of Phlogiston, which exerted so profound an influence for a century after his death, and he wrote :— " I wist that I have got hold of my pitcher by the right handle, for the pseudo-chemists seek gold, but I have the true philosophy, science, which is more precious."

At this critical period what was Boyle doing when the theory of Phlogiston dawned in the mind of the metallurgist Becher ? In 1672 Boyle wrote his paper on " Fire and Flame Weighed in the Balance," and came to the conclusion that the "ponderous parts of flame " could pass through glass to get at melted lead contained in a closed vessel. It has been considered strange that he did not interpret the experiment correctly, but he, like the phlogistic chemists, tried to show that the *subtilis ignis,* the material of fire or phlogiston, would penetrate all things, and could be gained or lost by them. Moreover, his later experiments showed him that glass was powerless to screen iron from the "effluvium of a loadstone." His experiment with lead heated in a closed glass vessel was a fundamental one, to which his mind would naturally revert if he could come back now and review the present state of our knowledge in the light of the investigations which have been made in the two centuries that have passed since his own work ceased. If he turned to the end of the first century after his death, he would see that the failure to appreciate the work of predecessors was as prevalent in the eighteenth century as in the sixteenth. The spirit of intolerance which led Paracelsus to publicly burn, in his inaugural lecture at Basle, the works of Galen, Hyppocrates, and Avincenna, survived in the eighteenth century when Madame Lavoisier burnt the works of Stahl, but it was reserved for the nineteenth century to reverently gather the ashes, recognising that when the writers of the School of Becher spoke of Phlogiston they meant what we understand by potential energy.

If Boyle, finding that the Fellows of the Royal Society had not carried out their intention to build a " Repository and Laboratory," sought the School of Mines and came to the Royal College of Science, he would surely thank my colleague, Professor Thorpe, for his vigorous defence last year, as President of this Section, of the originality of the work of Priestley and Cavendish, to which Boyle's own researches had directly led. We, on our part, remembering Berzelius's view that " oxygen is the centre point round which chemistry revolves," would hope to interest him most by selecting the experiments which arose out of the old metallurgical operation of separating the precious metals from lead by "cupellation." When, in conducting this operation, lead is heated in the presence of air it becomes converted into a very fluid dross. Boyle had, in 1661, taken this operation as the very first illustration to his " Sceptical Chemist " in proof of his argument as to the elemental nature of metals. He would remember the quantitative work of Geber in the eighth century, who stated that the lead so heated in air acquired a " new weight," and he would appreciate the constant reference to the operation of cupellation from the close of the sixth century, B.C., when the prophet Jeremiah wrote, to the work of Jean Rey in 1629, whose conclusions he would wish he had examined more closely. Lord Brouncker, as first President of the Royal Society, had called attention to the increase in weight of the lead in the " coppels " in the Assay Office in the Mint in the Tower, and Mayo had shown that the increase in weight comes from a distinct " *spiritus* " in the air. Boyle would incidentally see that Newton had accepted office in the Mint, where he doubtless continued his experiments on calcination begun some time before, and, as if to mark his interest in the operation of assaying, figures are represented on a bas-relief on his tomb in Westminster Abbey as conducting cupellation in a muffle. The old work merges wonderfully into the new. Chevreul, in the nineteenth century, confirms Otto Tachens' view in the seventeenth, as to the saponifying action of litharge. Deville employs molten litharge to absorb oxygen dissociated from its compounds, and Graham, by extracting occluded gases from iron and other metals, proves the accuracy of the old belief that elastic fluids can freely permeate even solid metals.

We may imagine with what vivid interest Boyle would turn, not merely to the results of Priestley's work, but to his methods. Priestley had decomposed litharge with the electric spark, and had satisfied himself in 1774, by heating red-lead, that the gas he obtained in his earlier experiments was really the one now called oxygen.

Boyle would see that in the period 1774-7 Lavoisier, being attracted by the " sceptical chemist's " own experiment on the heating of lead in closed vessels, overthrew the Phlogistic theory and placed chemistry on a firm basis by showing that the increase in weight of lead and tin, when heated in air, represents exactly the weight of the gaseous body added, and, finally, Dalton having developed the atomic theory and applied it to chemistry, Berzelius made lead memorable by selecting it for the first determination of an atomic weight.

Without diverting his attention from the phenomena of oxidation, Boyle would find questions the interest of which is only equalled by their present obscurity. He would contemplate the most interesting phase of the history of chemical science, described by Van t' Hoff as that of its evolution from the descriptive to the rational period, in the early days of which the impossibility of separating physics and chemistry became evident, and Boyle would find that chemistry is now regarded from the point of view of the mechanics of the atoms.

Deville's experiments on dissociation have rendered it possible to extend to the groups of atoms in chemical systems the laws which govern the fusion and vapourisation of masses of matter, and this has produced a revolution comparable in its importance to that which followed the discovery of the law of definite proportions, for dissociation has shown us that true causes of chemical change are variations of pressure and of temperature. For instance, oxygen may be prepared on an industrial scale from air by the intervention of oxide of barium heated to a constant temperature of 700° provided air be admitted to the heated oxide of barium, under a pressure of $1\frac{1}{2}$ atmospheres, while the oxygen thus absorbed is evolved if the containing vessel be rendered partially vacuous. It will be evident, therefore, that at a certain critical temperature and pressure the slightest variation of either will destroy the equilibrium of the system and induce chemical change.

The aim of Boyle's chemical writings was to show that no barrier exists between physics and chemistry, and to " serve the commonwealth of learning by begetting a good understanding betwixt the chemists and the mechanical philosophers," who had, as he said, " been too great strangers to each other's discoveries." In view of the dominant lines of research which occupy chemists at the present time, such, for instance, as the investigations of " Osmotic pressure " and of the application of Boyle's own law to salts in solution, he would feel that his hope had been realised, and that, though he lived a century too soon to take part in Berthollet's discussion with Proust, he nevertheless shares Berthollet's triumph in the long-delayed but now rapid development of chemistry as a branch of applied mechanics.

We need, however, no longer look at these questions from the point of view of Boyle, for our own interest in the application of chemical mechanics to metallurgy is sufficiently vivid, as instances to be given subsequently will show.

Hitherto I have mainly dwelt on questions relating to oxidation, but not less interesting is the history of the

steps by which an accurate knowledge was acquired of the other great process practised by the metallurgist, the one to which Paracelsus was the first to apply the name of "Reduction." Its explanation followed naturally from the elucidation of the phenomena of combustion by Lavoisier, who, in continuation of Macquer's experiments of 1771, proved, in conjunction with other workers, that carbonic anhydride is produced when the diamond is burnt in air or oxygen. Carbon has been known for ages as the most important of the reducing agents, but when, in 1772, Lavoisier heated oxide of lead and carbon together, he did not at first recognise that carbonic anhydride had been produced, simply because the volume of the gas set free was the same as if oxygen merely had been liberated. He soon, however, saw that neither the carbon alone, nor the oxide of lead alone, gave rise to the evolution of carbonic anhydride, which resulted from the *mutual action* of carbon and a constituent of the litharge. "This last observation leads us insensibly," he adds, "to very important reflections on the use of carbon in the reduction of metals." It most certainly did, and by 1815 an accurate, if incomplete, view of reduction had passed into the encyclopædias. It was seen that the removal of oxygen from burnt metals by carbon, "give the metals," as Fourcroy and Vauquelin put it, "a new existence." Some ten years later Le Play attempted to show that reduction is always effected by the intervention of carbonic oxide, which elicited the classical rejoinder from Gay-Lussac, who pointed out that "carbon alone, and at very moderate temperatures, will reduce certain metallic oxides without the intervention of carbonic oxide or of any other elastic fluid." I mention these facts because metallurgists are slow to recognise their indebtedness to investigators, and too often ignore the extreme pains with which an accurate knowledge has been acquired of the principles upon which their processes have been based.

The importance of a coherent explanation of reduction in smelting pig-iron is enormous. The largest blast-furnaces in 1815 hardly exceeded those in use in the previous century, and were at most only 40 feet high with a capacity of 5000 cubic feet. At the present day their gigantic successors are sometimes 90 feet high with a capacity of 25,000 cubic feet. This development of the blast-furnace is due to the researches of a number of investigators, among whom Von Tunner, Lowthian Bell, and Gruner deserve special mention. We are, however, forcibly reminded of the present incompleteness of our knowledge of the mechanism of reduction, when we remember that the experiments of H. P. Baker have led us to believe that pure carbon cannot be burnt in perfectly dry and pure oxygen, and therefore that the reducing agent, carbonic oxide, cannot be produced at all unless moisture be present.

Ludwig Mond, Langer, and Quincke, teach us not only that nickel can separate carbon from carbonic oxide, but the wholly unexpected fact that dry carbonic oxide can at a temperature of 100° take up nickel, which it again deposits if heated to 150°. Mond and Quincke, and independently Berthelot, have since proved the existence of the corresponding compound of iron and carbonic oxide, and it may safely be concluded that in the blast-furnace smelting iron this peculiar action of carbonic oxide plays an important part, and it doubtless aids the carburisation of iron by cementation. It is truly remarkable that the past year should have brought us so great an increase in our knowledge of what takes place in the reduction of an oxide of iron, and in the carburisation of the liberated metal. My own experiments have, I trust, made it clear that iron can, at an elevated temperature, be carburised by the diamond *in vacuo*; that is, in the absence of anything more than "a trace" of an elastic fluid or of any third element. Osmond has further shown, within the last few months, that the action between iron and carbon is a mutual one; for though carbon in the pure diamond form carburises iron, the metal in its turn, at a temper-

ature of 1050°, attacks the diamond, invests it with a black layer, and truly unites with it.

The question of the direct carburisation of iron (Darby's process) by filtering the molten metal through carbon, promises to be of much importance, for at present, as is well known, two millions of tons of steel which are made in the Bessemer converter in this country alone, are recarburised after "the blow" by the addition of spiegeleisen.

Carbonic oxide, moreover, would appear to be more chemically active than had been supposed; for during the present year Berthelot has shown that the perfectly pure gas heated to 500° or 550° produces carbonic anhydride with deposition of carbon at red heat, not by ordinary dissociation, but by decomposition preceded by polymerisation. He further shows that carbonic oxide will decompose ammoniacal nitrate of silver, and thus brings it into close connection with the aldehyds.

(2.) In turning to the modern aspects of metallurgical practice, we shall see that the whole range of the metallurgist's field of study is changing. It is no longer possible for him to devise a series of operations on the evidence afforded by a set of equations which indicate the completion of an operation; he has, as I have already suggested, to consider the complicated problems which have been introduced into chemistry from the sciences of physics and mechanics. He has, in fact, no longer to deal merely with atoms and molecules, but with the influence of mass. As Ostwald points out, we are reminded that many chemical processes are reciprocating so that the original products may be obtained from the product of the reaction. The result of such opposed processes is a state of CHEMICAL EQUILIBRIUM, in which both the original and the newly-formed substances are present in definite quantities that remain the same so long as the conditions, more especially temperature and pressure, do not undergo further change. Again, in very many metallurgical processes, reactions are rendered incomplete by the limitations imposed by the presence of bodies which cannot be speedily eliminated from the system, and the result may be to greatly retard the completion of an operation. The time has come when the principles of dynamic chemistry must be applied to the study of metallurgical problems if they are to be correctly understood, and it is, moreover, necessary to remember the part played by the surface separating the different aggregates in contact with one another. When, for instance, a reaction has to take place accompanied by the evolution of gas, there must be space into which the gas can pass. The rate, therefore, at which change takes place will obviously depend on the state of division of the mass.

One of the most remarkable points in the whole range of chemistry is the action engendered between two elements capable of reacting by the presence of a third body. It may be, and this is the most wonderful fact of all, that merely a trace of a third body is necessary to induce reaction, or to profoundly modify the structure of a metal. H. Le Chatelier and Mouret have pointed out that in certain cases it is inaccurate to say that the third body causes the reaction to take place, because, after it has destroyed the inter-molecular resistances which prevented the reaction taking place, the third body ceases to intervene. This is apparently the case when platinum sponge effects the union of oxygen and hydrogen, or conversely, when very hot platinum splits up water vapour into its constituent gases. Future investigation will, it is to be hoped, show whether the platinum does not exert some direct action in both cases. We can no longer neglect the study of such questions from the point of view of their practical application. The manufacture of red-lead presents a case in point. In "drossing" molten lead the oxidation of the lead is greatly promoted by the presence of a trace of antimony, and conversely, in the separation of silver from molten lead, by the aid of zinc,

H. Roessler and Endelmann have recently shown that aluminium has a remarkable effect in protecting the zinc from loss by oxidation, and, further, the presence of one-thousandth part of aluminium in the zinc is sufficient to exert this protecting action on that metal. I am satisfied that if our metallurgists are to advance their industrial practice, they must, if I may use such an expression, persistently think in calories, and not merely employ the ordinary atomic " tools of thought." They will then be able to state what reactions can, under given conditions, take place ; to indicate those which will be completed ; and to avoid those that are impracticable.

In France, the country of so many great metallurgists, men like Le Chatelier and Ditte are doing admirable service, by bringing the results of the labours and teaching of Ste. Claire Deville within the range of practical men. And if I do not refer more specifically to their work it is for want of space and not of appreciation, but a few simple cases of reversible actions will perhaps make the subject clear. In the blast-furnace the main reducing agent, carbonic oxide, is produced from the solid fuel by the reaction $CO_2 + C = 2CO$, a reaction which is theoretically impossible because it is endothermic, and would be attended by absorption of heat. But heat external to the system intervenes, and acts either by depolymerising the carbon into a simpler form which can combine with oxygen of the CO_2 with evolution of heat, or, by dissociating carbonic anhydride, sets oxygen free which combines with the carbon. Reduction of oxide of iron in the blast-furnace is mainly effected by carbonic oxide according to the well-known reaction—

$$Fe_2O_3 + 3CO = 2Fe + 3CO_2.$$
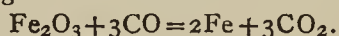
But the gas issuing from a blast-furnace contains carbonic oxide, an important source of heat. The view that this loss of carbonic oxide was due to the fact that the contact of the ore and the reducing gas was not sufficiently prolonged, led to a great increase in the height of blast-furnaces, but without, as Gruner showed, diminishing the proportion of carbonic oxide escaping from the throat. The reduction of an iron ore by carbonic oxide only takes place within certain well-defined limits, and a knowledge of the laws of chemical equilibrium would have saved thousands and thousands of pounds which have been wasted in building unduly high furnaces. I would add that large sums have also been sacrificed in the vain attempt to smelt oxide of zinc in the blast-furnace, for which operation patents have frequently been sought, in ignorance or defiance of the readiness with which the inverse action occurs, so that the reducing action of carbon on oxide of zinc may be balanced by the re-oxidation of the reduced zinc by carbonic anhydride, which is the product of the reduction. A further instance may be borrowed from an electro-chemical process which has been adopted for obtaining alloys of aluminium. As is well known, all attempts to effect the direct reduction of alumina by carbon have failed, because the reaction—

$$2(Al_2O_3) + 3C = 4Al + 3CO_2,$$
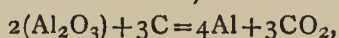
requires 783·2 calories, while only 291 calories would result from the conversion of carbon into carbonic anhydride, therefore the reaction cannot be effected ; but in Cowle's process aluminium is nevertheless liberated when alumina is mixed with charcoal and strongly heated by the passage of an electric current. This result is due, not to a simple reduction of alumina, but to its dissociation at the high temperature produced by the passage of a current of 1600 ampères between carbon poles, the liberated aluminium being at once removed from the system by metallic copper which is simultaneously present and may not be without action itself.

An instance of the importance of these considerations is presented in the manufacture of steel by the basic process. Much care is devoted to obtaining conditions which will ensure not only the elimination, but the order of the disappearance of the impurities from the molten pig-iron. In the basic process, as conducted in the closed converter, the phosphorus does not disappear until the carbon has left the fluid bath, whilst, when the open hearth furnace is used, the elimination of the phosphorus may be effected before that of the carbon, and it is asserted that if the carbon goes before the phosphorus is got rid of, a further addition of carbon is necessary. A curious and subtle case of chemical equilibrium is here presented. In the open hearth furnace and Bessemer converter respectively, the temperatures and pressures are different, and the conditions as to the presentation of oxygen to the fluid bath are not the same. The result is that the relative rates of oxidation of the phosphorus and carbon are different in the two cases, although in either case, with a given method of working, there must be a ratio between the phosphorus and carbon in which they disappear simultaneously. The industrial bearing of the question is very remarkable. In the basic Bessemer process the tendency of the phosphorus to linger in the bath renders an " after-blow " necessary, it may be only of a few seconds' duration, but much iron is nevertheless burnt and wasted, and Mr. Gilchrist tells me that if this after-blow could be avoided, a saving of some 6 per cent of the yield of steel would be effected annually, the value of which, at the present rate of output and price of steel, is no less than a quarter of a million sterling.

The volatilisation of sulphur in the converter while it is retained by the steel in the open-hearth furnace, and th increase in the percentage of manganese, which leaves the slag and returns to the bath of metal in the converter at the end of the " blow," will probably be traced to the disturbance of equilibrium which attends very slight variations in the conditions, especially as regards temperature and pressure, under which the operations are conducted.

In the blast-furnace the reducing action must be greatly dependent on the rate at which alkaline cyanides are formed, and Hempel has recently shown, by the aid of well-devised experiments, that the quantity of cyanides which may be obtained at a high temperature from carbon, nitrogen, and alkaline oxides, increases as the pressure becomes greater.

Metallurgical chemistry is, in fact, a special branch of chemical science which does not come within the ordinary sphere of the academic teaching of chemistry. It is often urged that metallurgical practice depends upon the application of chemical principles which are well taught in every large centre of instruction in this country, but a long series of chemical reactions exist which are of vital importance to the metallurgist, though they are not set forth in any British manual of chemistry, nor are dealt with in courses of purely chemical lectures. I feel bound to insist upon this point, because, as Examiner in Metallurgy for the Science and Art Department, I find that purely analytical and laboratory methods are so often given in the belief that they are applicable to processes conducted on a large scale, and at high temperatures.

We are told that technical instruction should be kept apart from scientific education, which consists in preparing the student to apply the results of past experience in dealing with entirely new sets of conditions ; but it can be shown that there is a whole side of metallurgical teaching which is truly educational, and leads students to acquire the habit of scientific thought as surely as the investigation of any other branch of knowledge.

It is, in fact, hardly possible, in a course of theoretical chemistry, to devote much attention to specific cases of industrial practice in which reactions are incomplete, because they are limited by the presence of bodies that cannot be directly eliminated from the chemical system. Take, for instance, the long series of reactions studied by Plattner, who published the results of his investigations in his celebrated treatise, " Die Metallurgische Röstprozesse," Freiberg, 1856, whose work I have chosen as a starting-point on account of our presence in South Wales near the great copper smelting district of Swansea. A complex sulphide, of which copper is the main metallic

constituent, contains some 50 ounces of silver to the ton. The problem may be supposed for the present to be limited to the extraction of the precious metal from the mass in which it is hidden, and the student deriving his knowledge from an excellent modern chemical treatise would find the case thus stated :—

" *Ziervogel's process* depends upon the fact that when argentiferous copper pyrites is roasted, the copper and iron sulphides are converted into insoluble oxides, whilst the silver is converted into a soluble sulphate, which is dissolved out by lixiviating the roasted ore with hot water, the silver being readily precipitated from this solution in the metallic state."

It is certain that if an observant, chemically-trained student visited a silver extraction works, and possessed sufficient analytical skill to enable him to secure evidence as to the changes that occur, he would find a set of facts which his training had not enabled him to predict, and he would establish the existence of a set of reactions to the nature of which his chemical reading had hardly given him a clue. The process to be considered is a simple one, but it is typical, and applies to a large proportion of the 7,000,000 ounces of silver annually obtained in the world from cupriferous compounds. He would be confronted with a ton or more of finely divided material spread in a thin layer over the bed of a reverberatory furnace. Suppose the material is what is known as a complex regulus as imported into Swansea or produced at Freiberg, to which are added rich native sulphides. The mixture then consists of sulphides mainly of iron and copper, with some sulphide of lead, and contains fifty or sixty ounces of silver to the ton, and a few grains of gold. It may also contain small quantities of arsenic and antimony as arsenides, antimonides, and sulpho-salts, usually with copper as a base.

The temperature of the furnace in which the operation is to be performed is gradually raised, the atmosphere being an oxidising one. The first effect of the elevation of the temperature is to distil off sulphur, reducing the sulphides to a lower stage of sulphurisation. This sulphur burns in the furnace atmosphere to sulphurous anhydride (SO_2), and coming in contact with the material undergoing oxidation, is converted into sulphuric anhydride (SO_3). It should be noted that the material of the brickwork does not intervene in the reactions, except by its presence as a hot porous mass, but its influence is, nevertheless, considerable. The roasting of these sulphides presents a good case for the study of chemical equilibrium. As soon as the sulphurous anhydride reaches a certain tension, the oxidation of the sulphide is arrested, even though an excess of oxygen be present, and the oxidation is not resumed until the action of the draught changes the conditions of the atmosphere of the furnace, when the lower sulphides remaining are slowly oxidised, the copper sulphide being converted into copper sulphate mainly by the intervention of the sulphuric anhydride formed as indicated. Probably by far the greater part of the iron sulphide only becomes sulphate for a very brief period, being decomposed into the oxides of iron, mainly ferric oxide, the sulphur passing off. Any silver sulphide that is present would have been converted into metallic silver at the outset, were it not for the simultaneous presence of other sulphides, notably those of copper and of iron, which enables the silver sulphide to become converted into sulphate. The lead sulphide is also converted into sulphate at this low temperature. The heat is now raised still further with a view to split up the sulphate of copper, the decomposition of which leaves oxide of copper. If, as in this case, the bases are weak, the sulphuric anhydride escapes mainly as such ; but when the sulphates of stronger bases are decomposed the sulphuric anhydride is to a great extent decomposed into a mixture of sulphurous anhydride and oxygen. The sulphuric anhydride, resulting from the decomposition of this copper sulphate, converts the silver into sulphate,

and maintains it as such, just as, in turn, at a lower temperature, the copper itself had been maintained in the form of sulphate by the sulphuric anhydride eliminated from the iron sulphide. When only a little of the copper sulphate remains undecomposed, the silver sulphate begins to split up, and the furnace charge must therefore be immediately withdrawn, or the whole of the silver sulphate would be converted into metallic silver, partly by the direct action of heat alone, and partly by reactions such as those shown in the following equations :—

$$Ag_2SO_4 + 4Fe_3O_4 = 2Ag + 6Fe_2O_3 + SO_2,$$
$$Ag_2SO_4 + Cu_2O = 2Ag + CuSO_4 + CuO.$$
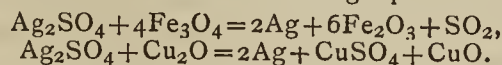
If the charge were not withdrawn, the silver would thus be effectually removed from the solvent action of water, and the smelter's efforts would have failed entirely. The charge still contains lead sulphate, which cannot be completely decomposed at any temperature attainable in the roasting furnace, except in the presence of silica, and it is well to leave it where it is if the residue has subsequently to be smelted with a view to the extraction of the gold. The elimination of arsenic and antimony gives rise to problems of much interest, and again confronts the smelter with a case of chemical equilibrium. For the sake of brevity it will be well for the present to limit the consideration to the removal of antimony, which may be supposed to be present as sulphide. Some sulphide of antimony is distilled off, but this is not its only mode of escape. An attempt to remove antimony by rapid oxidation would be attended with the danger of converting it into insoluble antimoniates of the metals present in the charge. In the early stages of the roasting it is therefore necessary to employ a very low temperature, and the presence of steam is found to be useful as a source of hydrogen, which removes sulphur as hydrogen sulphide, the gas being freely evolved. The reaction—

$$Sb_2S_3 + 3H_2 = 3H_2S + 2Sb,$$
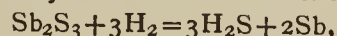
between hydrogen and sulphide of antimony is, however, endothermic, and could not, therefore, take place without the aid which is afforded by external heat. The facts appear to be as follows :—sulphide of antimony, when heated, dissociates, and the tension of the sulphur vapour would produce a state of equilibrium if the sulphur thus liberated were not seized by the hydrogen and removed from the system. The equilibrium is thus destroyed and fresh sulphide is dissociated. The general result being that the equilibrium of the system is continually restored and destroyed until the sulphide is decomposed. The antimony combines with oxygen and escapes as volatile oxide, as does also the arsenic, a portion of which is volatilised as sulphide.

The main object of the process which has been considered is the formation of soluble sulphate of silver. If arsenic and antimony have not been eliminated, their presence at the end of the operation would be specially inconvenient, as they give rise to the formation of arseniate and antimoniate of silver, insoluble in water, which may necessitate the treatment of the residues by an entirely different process from that which has hitherto been considered.

It will have been evident that effecting this series of changes demands the exercise of the utmost skill, care, and patience. The operations beginning at a dull red heat, or a temperature of some 500°, are completed at 700°, within a range, that is, of 200°. Judicious stirring has been necessary to prevent the formation of crusts of sulphates, which would impede the reactions, and, as has been shown, an undue elevation of temperature within a very limited range would, at any stage, have been fatal to the success of the operation. It is difficult to appreciate too highly the delicacy of sight and touch which enables an operator to judge by the aid of rough tests, but mainly from the tint of the streak revealed when the mass is rabbled, whether any particular stage has or has not been reached, and it will be obvious that the requisite skill is acquired solely by observation and experiment. The

technical instructor may impart information as to the routine to be followed and the appearances to be observed, but scientific knowledge of a high order can alone enable the operator to contend with the disturbing influences introduced by the presence of unexpected elements or by untoward variations in temperature. In the training of a metallurgist it is impossible to separate education from instruction, and the above description of a very ordinary operation will show the intimate relations between science and practice which are characteristic of metallurgical operations. Practice is dependent on science for its advancement, but scientific workers too often hesitate to attack metallurgical problems, and to devote the resources of modern investigation to their solution, because they are not aware of the great interest of the physical and chemical problems which are connected with many very simple metallurgical processes, especially with those that are conducted at high temperatures.

Proceeding yet one step further, suppose that the copper smelter takes possession of the residual mass, consisting mainly of oxide of copper, he would smelt it with fresh sulphide ores, and obtain, as a slag from the earthy matters of the ores, a ferrous silicate containing some small proportion of copper. The displacement of the copper from this silicate may be effected by fusing it with sulphide of iron, a fusible sulphide of iron and copper being formed which readily separates from the slag. By this reaction some 20,000 tons of copper are added to the world's annual production. Proceeding a step further, suppose the smelter to have reduced his copper to the metallic state. If arsenic had been originally present in the ore, and had not been eliminated entirely in the roasting, extraordinary difficulties will be met with in the later stages of the process, in extracting small quantities of arsenic which resist the smelter's efforts. Copper, moreover, containing arsenic cannot be "overpoled," as the presence of arsenic hinders the reducing action of gases on the copper. The amount of arsenic which the copper smelter has to remove may vary from mere traces up to 1 per cent, and if the copper is destined for the use of the electrical engineer, he will insist on its being as pure as possible, for the presence of a trace of arsenic would materially increase the electrical resistance of the copper, and would be fatal to its use in submarine telegraphy. If, on the other hand, the copper is intended for the maker of locomotive fire-boxes, he will encourage the retention of small quantities of arsenic, as it is found to actually increase the endurance of the copper, and the smelter will in such a case have no inducement to employ the basic furnace lining which Mr. Gilchrist has offered him, nor will he care to use the special methods for the removal of arsenic with which he is familiar. It may all seem simple enough, but the modern process of copper-smelting has been laboriously built up, and has a long and interesting pedigree which may be traced to at least the eighth century, when Geber described the regulus "coarse metal" as being "black mixed with livid," and our familiar "blue metal" as being "of a most clean and pleasant violet colour," and indicated the reasons for the difference.

(To be continued.)

ON NICKEL CARBON OXIDE AND ITS APPLICATION IN ARTS AND MANUFACTURES.

By LUDWIG MOND, F.R.S.

THE existence of a volatile compound of nickel and carbonic oxide was first discovered in my London laboratory in October, 1889, in the course of an investigation on which I was engaged with my assistants, Dr. Carl Langer

and Dr. Friedrich Quincke, into the remarkable property of metallic nickel to induce, at the comparatively low temperature of 350° C., the complete dissociation of carbonic oxide into carbon and carbonic acid, which, according to Victor Meyer and Carl Langer, by the application of heat alone remains incomplete at a temperature of 1690° C.

A very small quantity of nickel can effect the dissociation of a large quantity of carbonic oxide, and becomes converted into a very voluminous black mass containing varying quantities of carbon up to 85 per cent. This mass takes fire on exposure to air, so that we had to cool it under exclusion of air for the purpose of analysis, which was done in a slow current of carbonic oxide gas. This gas was subsequently led into a Bunsen burner, so as to keep it out of the atmosphere of the room. In this way we observed that when the cooling had proceeded to a certain point (about 150° C.), the Bunsen flame became luminous and remained so, and even became intenser, down to ordinary atmospheric temperature. When the gas before entering the burner was heated in a glass tube a metallic mirror was obtained, while the luminosity of the flame disappeared.

We were at first inclined to refer this phenomenon to the presence in the nickel of an unknown element, perhaps to Krüss and Schmidt's Gnomium, which at this time still haunted chemical literature. The metal of the mirror, however, gave all and every one of the reactions of nickel with remarkable brilliancy, and an approximate determination of the atomic weight came out so nearly to the very carefully-determined figure of Russel for nickel (58·58 as compared with 58·74), that there could be no doubt about its identity with our well-known old friend, whose character as a simple body, called in question by Krüss and Schmidt, was thus rehabilitated.

In repeating the experiment with carbonic oxide, quite free from hydrogen and moisture, and only contaminated with nitrogen, the same result was obtained. After removing the carbonic oxide by cuprous chloride, and heating the residual gas to 180° in aniline vapour, at which temperature nickel, quite free from carbon, is separated, we found the volume of the gas to expand considerably, and the gas to contain only nitrogen and carbonic oxide. It was thus evident that we had obtained a volatile compound of nickel and carbonic oxide, which, on heating, dissociated into its constituents. The increase of volume proved that one volume of gas yielded four volumes of carbonic oxide, and the determination of the amount of nickel deposited and the carbonic oxide formed led to a proportion of four equivalents of carbonic oxide to one of nickel. To further study the properties of this compound it was necessary to produce larger quantities, which took us a long time to accomplish. By preparing the nickel in a very fine state of division, at the lowest possible temperature, by reducing the oxide, or, better still, the oxalate, in a current of hydrogen at about 400° C., and by carefully purifying and regulating the current of carbonic oxide, we succeeded at last in forming the compound quite readily, and in obtaining a gas sufficiently rich that on passing it through a refrigerator, cooled by ice and salt, we condensed the compound to a liquid.

This liquid is colourless, mobile, highly refracting, possesses a characteristic odour, and is very volatile. It is soluble in a large number of organic liquids, such as alcohol, ether, chloroform, benzole, petroleum, tar oils, &c. It boils at 43° C. at 751 m.m. pressure without decomposition, and evaporates rapidly at ordinary temperature in a current of other gases. The specific gravity is 1·3185 at 17° C.; at −25° it solidifies, forming needle-shaped crystals; the pure vapour explodes when suddenly heated to above 60°, and even when the tube containing it is scratched roughly with a file. A mixture of the vapour with air explodes violently on the application of a flame. Both the liquid and the vapour are poisonous, the latter approximating carbonic oxide in this respect. According to an investigation kindly undertaken by Prof.

McKendrick, the liquid dissolved in chloroform produced, when injected subcutaneously in extremely small doses in rabbits, an extraordinary reduction of temperature, amounting in some cases to 12° C.

Careful determinations of the quantity of nickel contained in the liquid, made by introducing a weighed quantity into chlorine water and precipitation of the nickel from the resulting solution, led to figures agreeing very closely with the formula $Ni(CO)_4$, viz., 34·33 and 34·25 per cent of nickel, the formula requiring 34·28. The vapour density determined by Victor Meyer's method at 50° was found equal to 6·01 ; the formula $Ni(CO)_4$ requires 5·89.

The compound is chemically very inactive ; generally speaking, it only reacts with substances having a considerable affinity for nickel, such as the halogens, sulphur, oxygen, and oxidising substances, which combine with the nickel and liberate carbonic oxide. Chlorine and bromine when used in excess also enter into combination with the carbonic oxide. Sulphur in the dry state forms a sulphide of nickel corresponding to the formula Ni_2S_3, and dissolved in bisulphide of carbon it forms a sulphide containing more sulphur, but of varying composition. Selenium acts similarly but very slowly. Tellurium shows hardly any action. Metals (even potassium) are not acted upon.

Alkalies and acids (even strong hydrochloric acid) produce no change except they are oxidising agents, such as nitric acid and aqua regia. With metallic salts no reaction is obtained unless they have oxidising properties as hypochlorites, which form a higher oxide of nickel, or they are capable of giving off sulphur, such as hyposulphites and bisulphites.

We have tried in vain to substitute the carbonic oxide in this compound by other bivalent groups, or to introduce the carbonic oxide by means of this compound into organic substances. Our experiments in this direction have covered a very wide range and have included, amongst others, the following :—hydroxylamine hydrochloride, phenylhydrazin hydrochloride hydroxylamine, dichloracetic acid, tetrabromphenolbromide, ethylinechloride, and aceto-acetic-ether, but in no single instance have we succeeded in obtaining the desired result.

On exposure to moist or dry air a flocculent substance, which varies in colour from a light green to a dark brown, is very slowly formed. This substance dissolves completely in dilute acids with evolution of carbonic acid ; numerous analyses have not led to a definite proportion between Ni and CO_2 in this compound. On heating it to dull red heat it turns black. Prof. Berthelot, in a paper recently communicated to the French Academy of Sciences, assumes that this black colour is produced by the separation of carbon, and bases upon this an argument that the compound is of a complex composition, and that the nickel carbon oxide, on exposure to air, behaves like a real compound radical analogous to organo-metallic radicals. As, however, the black substance so obtained dissolves in dilute acids without leaving any residue, and as an exactly similar black substance is obtained by heating precipitated nickel carbonate, this argument does not seem to be conclusive, and I must regret that Professor Berthelot has not substantiated so important a conclusion by a complete analysis of the black substance.

Prof. Berthelot describes in the same paper a very beautiful blue compound obtained by treating nickel carbon oxide with nitric oxide. Unfortunately he does not publish an analysis of this beautiful substance either, so that until he has done so we are unable to judge of its bearing on the constitution of nickel carbon oxide.

With a view to elucidate this constitution I have, in conjuction with Prof. R. Nasini, of Rome, studied the physical properties of the liquid, more especially its refraction and dispersion. The details of this investigation have been communicated to the Accademia dei Lincei at Rome, and have also been published in the *Journal für Physikalische Chemie.*

We have determined the freezing-point of a dilute solution in benzol containing 4·8991 per cent, and have found the coefficient of diminution 0·2776, corresponding to a molecular weight of 176·5 ; while nickel carbon oxide requires 170·6. The mean cubical coefficient of expansion between 0° and 36° C. we found equal to 0·001853, which is one of the highest coefficients of expansion yet found for any liquid, and is only slightly exceeded by ethylic ether, ethyl chloride, and silicium tetrachloride. We have determined the refraction, and the dispersion for the lines α, β, and γ of hydrogen, and for the lines of lithium, sodium, and thallium, at three different temperatures, and have found both to be very high. The dispersion is about the same as carbon disulphide. The refraction varies very much with the temperature, the amount of variation being very nearly equal to that of carbon disulphide. The refraction for the D line at 10° C. is 1·45843.

According to Gladstone's formula this leads to the specific refraction of 0·3437, and the molecular refraction of 58·63. Under the supposition that the group CO had the same value in our compound which results from the sum of the atomic refraction of carbon and that of the divalent oxygen molecule in organic compounds, which is the more probable, as the group CO shows very nearly the same molecular refraction in compounds of the most different constitution, such as oxalic acid, ketones, and carbonyldichloride, the atomic refraction of nickel would come out equal to 25·02. This figure is very much higher, nearly two and a half times as high as it is in nickel salts, in which it has been found by Gladstone to be about 10 ; and about four times as high as the atomic refraction of metallic nickel as determined by Kundt and Dubois and Rubens, viz. about 6.

This difference of the atomic refraction of nickel in our compound and in its ordinary combinations is by far greater than that found in any other element. According to the generally accepted view, such differences are due to the element exercising a larger number of valencies, and are proportional to the number of valencies thus exercised. Nickel is generally bivalent. Its very high atomic refraction in nickel carbon oxide would thus lead to the conclusion that in this compound the nickel exercises a considerably higher valency than two, and that it has probably reached its maximum of saturation foreseen by Mendeléeff, who placed this metal in the eighth group of his Periodic System, to be equal to eight ; so that the constitution of our compound would be a simple combination of one octovalent equivalent of nickel with four bivalent equivalents of carbonic oxide, or that of nickel tetracarbonyl.

All that we definitely know of the chemical properties of the compound is in accord with this view of its constitution.

A determination of the magnetic rotary power of the compound kindly made by Dr. W. H. Perkin has shown this to be quite as exceptional as its refraction, and, with the exception of phosphorus, greater than any substance he has yet examined.

Professor Quincke, of Heidelberg, has had the kindness to investigate the magnetic properties of the liquid. He found the constant of diamagnetism at—

$$16° \text{ C. } k = -3·131 \times 10^{-10}$$

for magnetic fields of 6000 to 14,000 C.G.S. units. This is nearly the same as the constant for ethylic ether $= -3·218 \times 10^{-10}$.

The liquid is an exceptionally bad conductor of electricity. Up to 40 volts no current was observed to pass, the electrodes of 1 sq. c.m. area being 1 c.m. apart.

The highly interesting properties of nickel carbon oxide naturally led us to try whether we could not obtain similar compounds of other metals. It seemed a foregone conclusion that cobalt, in every respect so much like nickel, must give an analogous compound. It seemed probable that other metals of the eighth group, and those standing near to nickel in other groups, would also com-

bine with carbonic oxide. We tried a large number of elements, including osmium, palladium, ruthenium, rhodium, iridium, and manganese, by acting upon them in the finely divided state with carbonic oxide gas over a wide range of temperature. We tried it by double decomposition with numerous compounds, including zinc ethyl and mercury methyl; but, with one sole and single exception, without success.

This sole exception is iron. This metal, too, had for a long time given us negative results; but by preparing it at the lowest possible temperature by reduction of the oxalate in a current of hydrogen, and by acting upon this at about 80° C. with a very slow current of very pure carbonic oxide, I succeeded at last, in conjunction with Dr. F. Quincke, in obtaining evidence that a volatile compound of this element with carbonic oxide exists. The gas obtained imparted a yellow tinge to a Bunsen flame, and yielded slight metallic mirrors composed of pure iron. The quantity of the iron compound in the gas was, however, extremely small. By passing the gas through heavy tar oils, in which the compound is soluble, but from which it cannot be separated by fractionation, as it decomposes on heating the solution into iron and carbonic oxide before it volatilises, and by determining the iron and carbonic oxide so obtained, we ascertained, as far as the very small quantities of the substance at our disposal would allow, that it contained iron and carbonic oxide in the proportion of 1 equivalent of iron to 4·126 of carbonic oxide, or very nearly 1 to 4.

Since these results were communicated to the Chemical Society (18th June, 1891) I have continued the study of this body, in collaboration with Dr. Carl Langer, and we have arrived at obtaining it as an amber-coloured liquid, which, on standing, deposits tabular crystals of a darker colour, and solidifies entirely below −21° C. to a mass of needle-shaped crystals. It boils at 102° C., but leaves a small quantity of green-coloured oil behind.

We have made several analyses and vapour density determinations, but are not yet certain whether we have a pure substance in hand or a mixture of several iron carbonyls. We hope to be able very shortly to publish a full account of this interesting substance, which differs considerably in its chemical behaviour from nickel carbon oxide.

The fact that under ordinary circumstances nickel alone is acted on when a mixture of this metal with any other metallic or mineral substances is treated by carbonic oxide gas, led me to institute experiments to ascertain whether it would not be possible by means of carbon oxide to extract nickel direct from its ores, and such metallurgical products as nickel speiss and nickel matte. As the nickel is volatilised at the ordinary temperature in the form of a vapour disseminated through other gases from which it can be deposited without first condensing the nickel compound by simply heating these gases to the moderate temperature of 200° C., as it is thus obtained in the form of bright coherent masses of great purity, as the carbonic oxide used is completely liberated and can be employed over and over again, and as small quantities of the poisonous nickel compound which may escape decomposition would thus never leave the closed apparatus in which the process would be carried out, it seemed probable that such a process might be capable of industrial application, and might prove more economical than the very complicated operations metallurgists have now to resort to to produce tolerably pure nickel.

Experiments carried out under my instructions by Dr. Langer with a great variety of nickel ores from all parts of the world, containing from 4 to 40 per cent of nickel, as well as a number of samples of nickel speiss and nickel matte, have proved that as long as the nickel is combined with arsenic or sulphur the process is entirely successful on a laboratory scale. In the majority of cases I have been able to extract the nickel almost completely in three to four days.

Such ores or matte or speiss have in the first instance

to be calcined, so as to convert the nickel completely into oxide. The mass is then reduced in a current of hydrogenous gases, in practice water-gas, at a temperature of 450° C. It is cooled down to ordinary temperature, and treated with carbonic oxide in a suitable apparatus. For this purpose any good apparatus for treating solids by gases, of which a great number are in common use, will answer. Methodical apparatus moving the reduced ore in opposite direction to the current of carbonic oxide, at the same time exposing fresh surfaces, facilitate the operation. After a certain time the action of the carbonic oxide upon the nickel becomes sluggish. The mass is then heated to about 350° C. in a current of carbonic oxide, which regenerates the activity of the nickel. This may be done in the same apparatus, but it is preferable to use a separate apparatus connected with the first, and from which it is returned to the first by mechanical means, so that each apparatus can be kept at the same temperature. The carbonic oxide gas can be employed dilute, as it is obtained from gas-producers; but, since it is continuously recovered, a purer gas—such as can be cheaply prepared by passing carbonic acid through incandescent coke—is more advantageous, as it extracts the nickel more quickly and requires smaller apparatus. The gas charged with the nickel compound leaving the apparatus is passed through tubes or chambers heated to about 200° C., in which the nickel is deposited. The gas leaving these tubes is returned to the first apparatus and circulates continuously. From time to time the nickel is removed from the tubes in which it has been deposited. To facilitate this operation thin nickel sheets, bent to fit the tubes, are inserted, on which the nickel deposits, and which are easily taken out. The metal so obtained is almost chemically pure; only very rarely, in the case of certain ores, it is slightly contaminated with iron. Its density is equal to that of ordinary sheet nickel. Its mechanical properties still await investigation.

As the nickel is deposited in perfectly coherent films upon heated surfaces exposed to the gas containing the nickel carbon oxide, I have found it possible to produce direct from such gas articles of solid nickel or goods plated with nickel resembling in every way those obtained by galvanic deposition of metals, and reproducing with the same exactitude and fineness any design upon such articles.

This result can also be obtained by immersing heated articles in a solution of nickel carbon oxide in such solvents as benzol, petroleum, tar oils, &c., or by applying such solution to the heated articles with a brush or otherwise.

These processes open up a wide perspective of useful application, considering the many valuable properties of nickel, especially its power of resisting atmospheric and other chemical influences.

CONTRIBUTIONS TO MICRO-CHEMICAL ANALYSIS.*

By H. BEHRENS.

(Continued from p. 76).

XIX.—*Calcium.*

1. PRECIPITATION as sulphate occurs most frequently. It separates as $CaSO_4 + 2H_2O$ in prismatic crystals of the monoclinar system, which, in strongly acid liquids, fall down in thin, acicular crystals, entangled together in bushes and stars; in neutral solutions, or in the presence of acetic acid, they take the appearance of natural crystals of selenite, of the form of parallelograms, with an acute angle of 65° 36', and as swallow-tailed twin crystals, which in very dilute solutions, when concentrated by

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evaporation, accumulate along the margin. The limit of the reaction is about 0·00004 m.grm. Ca.

Hydrochloric and sulphuric acids diminish the sensitiveness, and in very dilute calcium solutions large quantities of alkaline salts must be avoided. Aluminium, chromium, and iron chlorides delay the reaction, and cause the production of small squares and granules of 10 micro. This may be remedied by boiling up with sodium or ammonium acetate. Boric acid interferes in a similar manner.

2. With potassium and sodium double tartrate and a little acetic acid, we obtain crystals of the form of strontium tartrate which often reach 80 micro. in length and 60 micro. in thickness. Limit of the reaction at 0·00003 m.grm. Ca.

Barium and strontium must be removed by means of sulphuric acid. Barium would disturb the formation of crystals, and strontium would yield mixed crystals with calcium. A separation of crystals of gypsum does not interfere. They re-dissolve, and in their place there appear large crystals of tartrate. In this form the reaction can be used as a check upon No. 1. Boric acid prevents the formation of crystals and occasions a finely granular turbidity. The action of aluminium, chromium, and iron chlorides is similar.

3. No precipitate is obtained in solutions of calcium salts. An excess throws down quadratic tables of a sparingly soluble double salt (20—25 micro.). A simultaneous addition of ammonium chloride causes the precipitate to appear in very dilute solutions. The limit of the reaction is at 0·000015 m.grm. Ca. Salts of strontium are not precipitated, barium falls only from very concentrated solutions in pale yellow rhombohedra (soluble in 38 parts of water).

4. With oxalic acid we obtain a very finely crystalline precipitate. In order to obtain at common temperatures crystals which are distinctly visible, the sample must be made moderately acid, preferably with nitric acid. The retarding action of the acid is less decisive with calcium than with strontium. The crystals of calcium oxalate are sharply-formed tetragonal pyramids of 12—25 micro. Limit of the reaction at 0·00006 m.grm. Ca. Boric acid and aluminium, chromium, and iron chlorides have little influence upon the precipitation. The influence of stannic chloride is much less manifest than with the barium and strontium oxalates.

5. Sodium bicarbonate occasions in solutions of calcium salts the formation of colourless rhombohedra of calcium carbonate, which polarise strongly. They increase rather sluggishly up to 25 micro. Ammonium carbonate produces a pulverulent precipitate which is gradually transformed into rhombohedra. The reaction is very sensitive, and it is not interfered with by aluminium, chromium, and iron. It is rather tedious, and it is useless in presence of magnesium, strontium, and barium.

XX.—*Lead.*

1. With hydrochloric acid. In the course of analytical operations lead is often unintentionally separated out as lead chloride, and it is then not always easy to recognise. From neutral solutions it is deposited in large rods or flat ridges, which often adhere together in the shape of an X and display ramifications. Lead chloride is soluble in 135 parts of water, its solubility being increased by nitric acid. Limit of the reaction at 0·0003 m.grm. Pb.

Potassium chloride causes a formation of thread-shaped rudimentary crystals. Ammonium chloride may entirely prevent the formation of crystals. If tin, bismuth, and antimony chlorides are present, water and hydrochloric acid dissolve only a part of the lead.

2. Potassium iodide can be used with advantage as a check upon the precipitation of lead chloride. Lead iodide generally falls down as a yellow crystalline powder. From its solution in hot water it crystallises in lemon-yellow six-sided tablets of 20 micro. Limit of the reaction 0·0002 m.grm. Pb.

In acid solutions of lead, antimony, and bismuth, potassium iodide determines not a yellow but an orange, or even a scarlet precipitate. Heating with dilute hydrochloric acid decomposes it and causes lead oxide to crystallise.

3. Lead sulphate can be caused to crystallise by slow evaporation with nitric acid. It forms acute rhombs of 10 micro., the edges of which are often indented, and six-sided tablets. Limit of the reaction at 0·00004 m.grm. Pb.

4. Sodium bicarbonate precipitates immediately, and ammonium carbonate in two minutes, ramified rods of 12—20 micro., the form of which is very striking and characteristic. Limit of the reaction at 0·00006 m.grm. Pb.

Oxalic acid throws down grains and crosses of 20—30 micro. (in presence of stannous chloride rosettes of 100 micro.)—but from hot solutions rectangular rods of 40—60 micro. The reaction has little value. Its limit is at c·0002 m.grm. Pb.

Potassium bichromate throws down from solutions of lead a yellow powder of $PbCrO_4$. Its finely granular texture and opacity render this precipitate unfit for microscopic observation.

XXI.—*Copper.*

1. With potassium nitrite and lead acetate. Black cubes with sharp edges of 10—25 micro., which, by recrystallisation, can be brought to 70 micro. In thin plates translucent, orange, or brown. Limit of reaction 0·00003 m.grm. Cu.

The sample to be tested for copper is placed in a drop of a concentrated solution of potassium nitrite, supersaturated with acetic acid, and a minute granule of lead acetate is added. A turbidity ensues, and in one to two minutes cubes of 10—25 micro. are formed. The new copper compound—the composition of which probably corresponds to that of potassium-nickel-lead nitrite—is decomposed by hot water. It is partially soluble in an acidified solution of potassium nitrite; another portion is decomposed, and is re-formed on cooling. Barium and strontium give analogous compounds which do not crystallise so well.

2. With potassium ferrocyanide there are obtained from ammoniacal solutions of copper during the evaporation of the ammonia, yellow crystalline structures generally feathery and dendritic. They gradually become red on exposure to the air, or immediately on the addition of acetic acid. Limit of reaction 0·0001 m.grm. Cu.

3. Ammonium mercuri-sulphocyanide precipitates from slightly acid solutions of copper brownish green crystals, which in form resemble those of cobalt-mercuric sulphocyanide. If the solution contains both metals, cobalt is separated first and then copper. No mixed crystals are formed. The limit of this characteristic but rather tedious reaction is 0·0001 m.grm. Cu.

4. Potassium iodide precipitates from concentrated solutions of cupric salts white pulverulent cuprous iodide, with a simultaneous separation of iodine. To dilute solutions there must be added at the same time a reducing agent (sodium sulphite and sulphuric acid). The finely granular texture of this precipitate makes the reaction inconvenient. Limit at 0·00005 m.grm. Cu.

XXII.—*Mercury.*

a. Mercurous Salts.—1. Hydrochloric acid throws down fine needles which quickly break up to minute granules of a square section. Mercurous chloride is blackened by ammonia. For its examination the precipitate should be illuminated from below. Limit 0·00025 m.grm. Hg.

2. Potassium bichromate produces in mercurous solutions containing a considerable quantity of free nitric acid a fine red pulverulent precipitate, which in the acid liquid is transformed (not invariably) into cruciform red crystals of 10—15 micro. Limit 0·0005 m.grm. Hg.

b. Mercuric Salts.—1. Potassium iodide precipitates

from mercuric solutions a scarlet deposit consisting of quadratic tablets and pyramids of a square section. In an excess of the reagent it dissolves to a colourless liquid. An addition of copper sulphate reproduces it more beautifully than before, unless a large excess of potassium iodide is present. Limit of reaction 0·000075 m.grm. Hg.

2. Stannous chloride reacts upon mercuric chloride very sensitively, but for microscopic use it is less to be recommended than potassium iodide, as the precipitate of mercurous chloride is very finely granular. Limit of the reaction 0·00005 m.grm. Hg.

3. Ammonium sulphocyanide throws down from concentrated solutions of mercuric salts a crystalline colourless precipitate soluble in excess. If cobalt nitrate is added there appear the dark blue crystals of cobalt-mercuric sulphocyanide, described under Cobalt 2. In very dilute solutions they appear at the margin of the drop during evaporation. Limit at 0·00004 m.grm. Hg. Lead and bismuth must not be present.

(To be continued).

CORRESPONDENCE.

SEPARATION OF THE HALOGENS.

To the Editor of the Chemical News.

Sir,—In studying the halogens some time ago I found that by putting $KI + MnO_2 + C_2H_4O_2$ into a test-tube and slightly heating, free I was liberated, and that—

$$KBr + MnO_2 + HNO_3$$
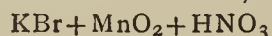
slightly heated yielded free Br. I then put together a crystal of KI, KBr, and $NaCl + MnO_2 + C_2H_4O_2$, and slightly heated, and obtained free I. After driving it all off I added a little HNO_3, and upon heating obtained free Br, which was driven off also, then *cooled* the tube, and cautiously added H_2SO_4, and heated, when free Cl came away, known by smell, colour, and bleaching of moist litmus. The experiment is interesting from the fact that it is held that these three elements cannot be recognised in the presence of one another.—I am, &c.,

MATTHEW FORBES.

12, Bell Street, Dundee.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxiii., No. 5, August 3, 1891.

Combustion and Formation-Heats of the Nitrobenzenes.—MM. Berthelot and Matignon.—Thermochemical determinations.

Improvements introduced in the Manufacture of Soda-Water. Arrangement of the Syphon.—M. de Pietra-Santa.—The water used is taken from the springs of the Dhuis and the Vanne, and is submitted to repeated filtration. The gasification is effected by means of liquid carbonic acid. The fittings of the syphon are formed of pure tin to the total exclusion of lead.

The Expansion of Phosphorus and its Change of Volume at the Melting-Point.—A. Leduc.—According to the author, phosphorus expands almost regularly up to the point of fusion, which is at 44·2° of the mercurial thermometer, and consequently at 44·1° of the normal thermometer. He has followed the expansion of the liquid phosphorus up to 50°, and then down to 26°, at which it solidified.

Study on the Chemical Neutralisation of Acids and Bases by Means of their Electric Conductivities.—Daniel Berthelot.—Potassa, a powerful base, yields with hydrochloric acid, acetic acid and phenol, compounds having conductivities near to each other, behaving like true salts, being stable in solution, and not decomposed by water. Ammonia forms with hydrochloric and acetic acid stable compounds, but with phenol it forms an instable compound less conductive than the neutral salts, and in great part dissociated by water. Aniline yields with hydrochloric acid a stable compound, which is a good conductor; with acetic acid an instable compound, moderately conductive; with phenol it forms merely a non-conductive mixture without a trace of combination.

Action of Phenylhydrazine upon the Phenols.—Alphonse Seyewetz.—A fairly great number of phenols react with phenylhydrazine. Among them the diatomic phenols seem to form such compounds most readily. Many analogous compounds of aniline and phenylhydrazine (aniline phenates) are known, but they do not correspond exactly with those furnished by phenylhydrazine. Several phenols combine very readily with aniline, but not with phenylhydrazine. Certain phenylhydrazine phenates are very easily formed, whilst the corresponding aniline phenates are often formed with great difficulty.

Action of Poisons upon the Germination of the Seeds of the Plants by which they are Produced.—Ch. Cornevin.—When a phanerogamous plant elaborates a poison by any part other than its seeds, if such poison is brought in contact for a sufficient time with the seeds, it sometimes hinders germination, *e.g.*, nicotine, and sometimes favours it as in the case of opium. Soil saturated with such substances, is either, according to the species, unfit for the development of the vegetable germ, or promotes it like a suitable manure.

Zeitschrift fur Analytische Chemie.
Vol. xxix., Part 6.

Recognition of a Fraudulent Addition of " Rubenkraut " in Rhenish Obst-Kraut.—(See page 74).

A Cheap Ebullioscope.—Benevolo (*Weinlaube*).—This instrument cannot be intelligibly described without the accompanying cut.

Detection of Sugar or Treacle in Roasted Coffee.—A. Stutzer and O. Reitmair (*Zeit. Angew. Chemie*).—Already inserted.

The Sophistications of Saffron.—G. Kuntze and A. Hilger (*Archiv fur Hygiene*).—Pure saffron should not contain more than 8 per cent of ash. Its ash yields 13·53 per cent of phosphoric acid, whilst safflower (*Carthamus tinctorius*) contains only about 2 per cent, and the flowers of *Calendula* 0·37 per cent.

Chemical Examination of Pepper.—H. Weigmann (*Repert. Anal. Chemie*).—This author is criticised as having in his researches omitted certain known and important precautions.

Detection and Estimation of Starch in Liquids containing Dextrine.—G. Burkard (*Chemiker Zeitung*).—Already inserted.

Detection of Magenta in Extracts of Dye-Woods.—F. Fairley.—From the *Jour. Soc. Chem. Ind.*

Determination of Phenols in Carbolic Soap.—A. H. Allen.—From the *Analyst.*

The Presence of Alcohol in Commercial Ethyl-Ether.—Th. Poleck and K. Thümmel (*Archiv. de Pharm.*).—Already inserted.

Determination of Paraffin, Ceresine, and Mineral Oils in Fats and Waxes.—F. M. Horn (*Zeit. Angew. Chemie*).—Already inserted.

Determination of Resin Oils in Mineral Lubricants.—L. Storch (*Chemiker Zeitung*).—Already inserted.

Detection of Cotton-Oil in Lard.—A. Bujard and J. Waldbauer (*Zeit. Angew. Chemie*).—Already inserted.

Rape Oil.—Reimer and Will (*Deutsch. Chem. Gesell.*).—Already inserted.

Recognition of Sesame Oils.—W. Bishop.—From the *Journal de Pharm. et de Chemie*.

Determination of Castor Oil in Oily Mixtures.—J. Braun (*Rundschau*).—The author submits a weighed sample to dry distillation in a tared distilling flask capable of holding 100 to 200 c.c. The heat is rapidly raised to 265°. After heating from 15—30 minutes, the mass suddenly swells up, when the flame is removed; the contents of the flask are allowed to cool from 50 to 60°, and then washed successively with 5 per cent ammonia, water, alcohol, and ether, shaking up the mass well. The weight of the residue if multiplied by 1·63 gives the weight of the castor oil.

Examination of Commercial Cocaine.

Determination of Colchicine in Colchicum Seeds.—Kremel (*Pharm. Post* and *Chemiker Zeitung*).—For these two papers we must refer to the original.

Distinction between Common Turpentine and Larch Turpentine.—E. Hirschsohn (*Pharm. Zeit. fur Russland*).—If a few drops of common turpentine in a test-tube are covered with 5 parts ammonia of specific gravity 0·96, the turpentine forms a milky emulsion and soon gelatinises. Larch, otherwise known as Venice turpentine, remains apparently unaffected, but if constantly stirred up it becomes a solid, colourless mass.

Determination of the Value of Strychnos Seeds and Preparations of Strychnine. — H. Beckurtz (*Archiv. der Pharm.*).—The author recommends the method of Dietrich given in this journal, vol. xxix., p. 231.

Valuation of Pomegranate Root Bark.—E. Aweng (*Pharm. Zeitung*).—For this paper the reader is referred to the original.

Recognition and Determination of Reducing Substances, Carbohydrates, and Sugars on Animal Liquids.—A compilation from a number of sources not admitting of abstraction.

Absorption Spectrum of Methæmoglobine and Sulphmethæmoglobine. — T. Araki (*Zeit. Physiol. Chemie*).—Of the four absorption bands ascribed to methæmoglobine, Araki considers only band I. in the red as characteristic. Bands II. and III. lying between D and E in the green are ascribed to an admixture of oxyhæmoglobine, and can be converted by cautious reduction (preferably by putrefaction in a sealed tube) into the broad absorption band of reduced hæmoglobine. In this case the solution shows the spectrum of hæmoglobine, which, on shaking with air, passes into oxyhæmoglobine. A solution of blood turned green by the introduction of hydrogen sulphide shows absorption beginning near C, and extending almost to D, interrupted by a lighter zone in the middle. Between D and E the solution, if oxygen can enter, shows the absorption bands of oxyhæmoglobine.

The Atomic Weight of Tellurium.—B. Brauner.—From the *Journal of the Chemical Society*.

The Atomic Weight of Zirconium.—G. H. Bailey.—From the CHEMICAL NEWS.

The Atomic Weight of Iridium.—A. Joly.—From the *Comptes Rendus*.

MISCELLANEOUS.

British Association for the Advancement of Science.—The following are the names of the Officers and Committee of Section B (Chemical Science) of the Cardiff Meeting of the British Association:—

President — Professor W. Chandler Roberts-Austen, C.B., F.R.S., F.C.S.

Vice-Presidents—Sir F. A. Abel, C.B., D.C.L., D.Sc., F.R.S; W. Crookes, F.R.S.; J. H. Gladstone, Ph.D., F.R.S.; Professor G. D. Liveing, M.A., F.R.S.; Professor H. M'Leod, F.R.S., F.C.S.; Professor R. Meldola, F.R.S.; Ludwig Mond, F.R.S., F.C.S.; Professor C. M. Thompson, M.A., D.Sc.

Secretaries—C. H. Bothamley, F.C.S., F.I.C.; H. Forster Morley, M.A., D.Sc., F.C.S. (*Recorder*); Dr. W. W. J. Nicol, M.A., F.R.S.E.; G. S. Turpin, M.A., D.Sc.

Committee—A. H. Allen; R. W. Atkinson; J. Brown; Professor W. R. Dunstan; A. E. Fletcher; G. Gladstone; A. Vernon Harcourt, F.R.S.; H. Heywood, J.P.; H. C. Jenkins; Dr. H. R. Mill; D. H. Nagel, M.A.; Dr. S. Rideal; Professor H. Lloyd Snape; T. Turner.

The Papers brought before the Section were as follows:—

President's Address.

Report of the Committee on International Standards for the Analysis of Iron and Steel.

Report of the Action of Light upon Dyed Colours.

Report on the Influence of the Silent Discharge of Electricity on Oxygen and other Gases.

Report on the Bibliography of Solution.

Report on the Nature of Solution,

Report on the Bibliography of Spectroscopy.

Report of the Committee on the Formation of Haloid Salts.

Prof. Vivian B. Lewes.—The Spontaneous Ignition of Coal.

Ludwig Mond, F.R.S.—Nickel Carbon Oxide and its Application in Arts and Manufactures.

W. Crookes, F.R.S.—Electrical Evaporation of Metals and Alloys,

T. Turner.—The Cause of the Imperfection of the Surface of Rolled Copper Alloys.

Prof. Roberts-Austen, F.R.S. — Certain Pyrometric Measurements, and Methods of Recording them.

A. P. Laurie.—On the Existence of a Compound in Alloys of Gold and Tin.

A. Vernon Harcourt, F.R.S., and F. W. Humphery.—The Relation between the Composition of a Double Salt and the Composition and Temperature of the Liquid in which it is Formed.

Dr. J. H. Gladstone, F.R.S., and W. Hibbert.—Some Experiments on the Molecular Refraction of Dissolved Electrolytes.

Prof. H. M'Leod, F.R.S. — The Action of Heat on Alkaline Hypochlorites.

W. Symons.—A Simple Apparatus for Storing Dry Gases.

Report on Isomeric Naphthalene Derivatives.

Report on Wave-Length Tables of the Spectra of the Elements.

Report on the Absorption Spectra of Pure Compounds.

Prof. W. C. Roberts-Austen, C.B., F.R.S., and Prof. A. W. Rücker, F.R.S.—The Specific Heat of Basalt.

Prof. F. Clowes. — An Apparatus for Testing Safety Lamps.

Prof. C. M. Thompson. — Didymium from Different Sources.

Prof. W. Ramsay, F.R.S.—The Nature of Solution.

C. H. Bothamley. — The Interpretation of certain Chemical Reactions.

J. J. Sudborough.—The Action of Nitrosyl Choride on Unsaturated Carbon Compounds.

W. E. Adeney.—Formation of Peaty Colouring Matters in Sewage by the Action of Micro-organisms.

C. G. Moor.—A New Nethod for the Disposal of Sewage.

A. H. Allen. — The Reaction of Glycerides with Alcoholic Potash.

H. C. Jenkins.—Note on Electrolysis of Alloys.

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ADDRESS TO THE CHEMICAL SECTION
OF THE
BRITISH ASSOCIATION.

By Professor W. C. ROBERTS-AUSTEN, C.B., F.R.S.,
President of the Section.

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CARDIFF, 1891.

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(3). THE foregoing instances have been given to indicate the general nature of metallurgical chemistry. It will be well now to show how the great advances in metallurgical practice have been made in the past, with a view to ascertain what principles should guide us in the future.

It is a grave mistake to suppose that in industry, any more than in art, national advance takes place always under the guidance of a master possessed of some new gift of invention; yet we have been reminded that we are apt to be reverent to these alone, as if the nation had been unprogressive, and suddenly awakened by the genius of one man. The way for any great technical advance is prepared by the patient acquisition of facts by investigators of pure science. Whether the investigators are few or many, and consequently whether progress is slow or rapid, will depend in no small measure on the spirit of the nation as a whole. A genius whose practical order of mind enables him to make some great invention suddenly arises, apparently by chance, but his coming will, in most cases, be found to have "followed hard upon" the discovery by some scientific worker of an important fact, or even the accurate determination of a set of physical constants. No elaborate monograph need have reached the practical man —a newspaper paragraph, or a lecture at a Mechanics' Institute may have been sufficient to give him the necessary impulse; but the possessors of minds which are essentially practical often forget how valuable to them have been the fragments of knowledge they have so insensibly acquired that they are almost unconscious of having received any external aid.

The investigating and the industrial faculty are sometimes, though rarely, united in one individual. Rapid advance is often made by those who are untrammelled by a burden of precedent, but it should be remembered that though the few successes, which have been attained in the course of ignorant practice, may come into prominence, none of the countless failures are seen.

I would briefly direct attention to certain processes which have been adopted since the year 1849, when Dr. Percy presided over this Section at Birmingham, a great metallurgical centre. In that year the President of the Association made a reference to metallurgy, a very brief one, for Dr. Robinson only said "the manufacture of iron has been augmented six-fold by the use of the puddling-furnace and the hot-blast, both gifts of theory"; and so, it may be added, are most of the important processes which have since been devised. Take the greatest metallurgical advance of all, the Bessemer process, which has probably done more than any other to promote the material advance of all countries. It was first communicated to the world at the Cheltenham Meeting of the British Association, 1856. Its nature is well known, and I need only say that it depends on the fact that when air is blown through a bath of impure molten iron, sufficient heat is evolved by the rapid combustion of silicon, manganese, and carbon to maintain the bath fluid after these elements have been eliminated, there being no external source of heat, as there is in the puddling furnace or the refinery hearth. We have recently been told that at an early and perilous stage of the Bessemer process confidence in the experiments was restored by the observation that the temperature of the "blown" metal contained in a crucible was higher than that of the furnace in which it was placed. The historian of the future will not fail to record that the way for the Bessemer process had been prepared by the theoretical work of Andrews, 1848, and of Favre and Silbermann, 1852, whose work on the calorific power of various elements showed that silicon and phosphorus might be utilised as fuel, because great heat is engendered by their combustion.

The basic process for removing phosphorus, a process of great national importance, the development of which we owe to Thomas and Gilchrist, is entirely the outcome of purely theoretical teaching, in connection with which the names of Gruner and Percy deserve special mention. In the other great group of processes for the production of steel, those in which Siemens's regenerative furnace is employed, we have the direct influence of a highly-trained theorist, who concluded his address as President of this Association in 1882 by reminding us that " in the great workshop of nature there is no line of demarcation to be drawn between the most exalted speculation and commonplace practice." The recent introduction of the method of heating by radiation is, of course, the result of purely theoretical considerations.

The progress in the methods of extracting the precious metals has been very great, both on the chemical and engineering sides, but it is curious that in the metallurgy of gold and silver, many ancient processes survive which were arrived at empirically—a noteworthy exception being presented by the chlorine process for refining gold, by the aid of which many millions sterling of gold have been purified. The late Mr. H. B. Miller based this process for separating silver from gold on the knowledge of the fact that chloride of gold cannot exist at a bright red heat. The tension of dissociation of chloride of gold is high, but the precious metal is not carried forward by the gaseous stream, at least not while chloride of silver is being formed.

The influence of scientific investigation is, however, more evident in that portion of the metallurgic art which deals with the adaptation of metals for use, rather than with their actual extraction from the ores.

Only sixteen years ago Sir Nathaniel Barnaby, then Director of Naval Construction, wrote, " our distrust of steel is so great that the material may be said to be altogether unused by private ship-builders . . . . and marine engineers appear to be equally afraid of it." He adds, " the question we have to put to the steel makers is, what are our prospects of obtaining a material which we can use without such delicate manipulation and so much fear and trembling?" All this is changed, for, as Mr. Elgar informs me, in the year ending on June 30 last, no less than 401 ships, of three-quarters of a million gross tonnage, were being built of steel in the United Kingdom.

Why is it, then, that steel has become the material on which we rely for our ships and for our national defence, and of which such a splendid structure as the Forth Bridge is constructed? It is because side by side with great improvement in the quality of certain varieties of steel, which is the result of using the open-hearth process, elaborate researches have shown what is the most suitable mechanical and thermal treatment for the metal; but the adaptation of steel for industrial use is only typical, as the interest in this branch of metallurgy generally appears for the moment to be centred in the question whether metals can, like many metalloids, pass under the application of heat or mechanical stress from a normal state to an allotropic one, or whether metals may even exist in numerous isomeric states.

It is impossible to deal historically with the subject now further than by stating that the belief in more than one "modification" is old and widespread, and was expressed by Paracelsus, who thought that copper "contains in itself its female, which could be isolated so as to give

"two metals" . . . . "different in their fusion and malleability," as steel and iron differ. Within the last few years Schützenberger has shown that two modifications of copper can exist, the normal one having a density of 8·95, while that of the allotropic modification is only 8·0, and is, moreover, rapidly attacked by dilute nitric acid which is without action on ordinary copper. It may be added that Lord Rayleigh's plea for the investigation of the simpler chemical reactions has been partly met, in the case of copper, by the experiments conducted by V. H. Veley on the conditions of chemical change between nitric acid and certain metals.

Bergmann, 1781, actually calls iron polymorphous, and says that it plays the part of many metals. "Adeo ut jure dici queat polymorphum ferrum plurium simul metallorum vices sustinere." Osmond has recently demonstrated the fact that at least two modifications of iron must exist.

Professor Spring, of Liége, has given evidence that in cooling lead-tin alloys polymerisation may take place after the alloys have become solid, and it seems to be admitted that the same cause underlies both polymerisation and allotropy. The phenomenon of allotropy is dependent upon the number of the atoms in each molecule, but we are at present far from being able to say what degree of importance is to be attached to the relative distance between the atoms of a metal or to the "position of one and the same atom" in a metallic molecule, whether the metal be alloyed or free, and it must be admitted that in this respect organic chemistry is far in advance of metallurgic chemistry. I cannot, as yet, state what is the atomic grouping in the brilliantly-coloured gold aluminium alloy, $AuAl_2$, which I have had the good fortune to discover, but in it the gold is probably present in the same state as that in which it occurs in the purple of cassius.

Much valuable information on the important question of allotropy in metals has already been gathered by Pionchon, Ditte, Moissan, Le Chatelier, and Osmond, but reference can only be made to the work of the two latter. Le Chatelier concludes that in metals which do not undergo molecular transformation the electrical resistance increases proportionally to the temperature. The same law holds good for other metals at temperatures above that at which their last change takes place—for example, in the case of nickel above 340°, and in that of iron above 850°.

It is probable that minute quantities of foreign matter which profoundly modify the structure of masses of metal also induce allotropic changes. In the case of the remarkable action of impurities upon pure gold I have suggested that the modifications which are produced may have direct connection with the periodic law of Mendeleeff, and that the causes of the specific variations in the properties of iron and steel may thus be explained. The question is of great industrial importance, especially in the case of iron; and Osmond, whose excellent work I have already brought before the members of this Association in a lecture delivered at Newcastle in 1889, has specially studied the influence upon iron exerted by certain elements. He shows that elements whose atomic volumes are smaller than that of iron delay, during the cooling of a mass of iron from a red heat, the change of the β, or hard variety of iron, to the α, or soft variety. On the other hand, elements whose atomic volumes are greater than that of iron tend to hasten the change of β to α iron. It is, however, unnecessary to dwell upon this subject, as it was dealt with last year in the Address of the President of the Association.

It may be added that the recent use of nickel-steel for armour plate, and the advocacy of the use of copper-steel for certain purposes, is the industrial justification of my own views as to the influence of the atomic volume of an added element on the mechanical properties of iron, and it is remarkable that the two bodies, silicon and aluminium, the properties of which when in a free state are so totally different, should, nevertheless, when they are alloyed with iron, affect it in the same way. Silicon and aluminium have almost the same atomic volumes.

The consequences of allotropic changes, which result in alteration of structure, are very great. The case of the tin regimental buttons which fell into a shapeless heap when exposed to the rigorous winter at St. Petersburg is well known. The recent remarkable discovery by Hopkinson of the changes in the density of nickel-steel (containing 22 per cent of nickel), which are produced by cooling to −30°, affords another instance. This variety of steel, after being frozen, is readily magnetisable, although it was not so before; its density, moreover, is permanently reduced by no less than 2 per cent by the exposure to cold, and it is startling to contemplate the effect which would be produced by a visit to the arctic regions of a ship of war built in a temperate climate of ordinary steel, and clad with some three thousand tons of such nickel-steel armour; the shearing which would result from the expansion of the armour by exposure to cold would destroy the ship. Experimental compound armour-plates have been made faced with 25 per cent nickel-steel, but it remains to be seen whether a similar though lessened effect would be produced on the steel containing 5 to 7 per cent of nickel, specially studied by J. Riley, the use of which is warmly advocated for defensive purposes. Further information as to the molecular condition of nickel-steel has within the last few weeks been given by Mercadier, who has shown that alloying iron with 25 per cent of nickel renders the metal isotropic.

The molecular behaviour of alloys is indeed most interesting. W. Spring has shown, in a long series of investigations, that alloys may be formed at the ordinary temperature, provided that minute particles of the constituent metals are submitted to great pressure. W. Hallock has recently given strong evidence in favour of the view that an alloy can be produced from its constituent metals with but slight pressure if the temperature to which the mass is submitted be above the melting-point of the alloy, even though it be far below the melting-point of the most easily fusible constituent. A further instance is thus afforded of the fact that a variation of either temperature or pressure will effect the union of solids. It may be added that B. C. Damien is attempting to determine what variation in the melting-point of alloys is produced by fusing them under a pressure of two hundred atmospheres. Italian physicists are also working on the compressibility of metals, and F. Boggio-Lera has recently established the existence of an interesting relation between the coefficient of cubic compressibility, the specific gravity, and the atomic weight of metals.

Few questions are more important than the measurement of very high temperatures. Within the last few years H. Le Chatelier has given us a thermo-couple of platinum with platinum containing 10 per cent of rhodium, by the aid of which the problem of the measurement of high temperatures has been greatly simplified. A trustworthy pyrometer is now at hand for daily use in works, and the liberality of the Institution of Mechanical Engineers has enabled me to conduct an investigation which has resulted in the adoption of a simple appliance for obtaining, in the form of curves, photographic records of the cooling of masses of metal. A report on the subject has already been submitted to a Committee, of which the Director-General of Ordnance Factories is the Chairman; and Dr. Anderson, to whom I am indebted for valuable assistance and advice, intends to add this new method for obtaining autographic curves of pyrometric measurements to the numerous self-recording appliances used in the Government factories which he controls. It has proved to be easy to ascertain by the aid of this pyrometer what thermal changes take place during the cooling of molten masses of alloys, and it is possible to compare the rate of cooling of a white-hot steel ingot at definite positions situated respectively near its surface

and at its centre, and thus to solve a problem which has hitherto been considered to be beyond the range of ordinary experimental methods. Some of the curves already obtained are of much interest, and will be submitted to the Section. It is probable that the form of the curve which represents the solidification and cooling of a mass of molten metal affords an exceedingly delicate indication as to its purity.

Prof. H. E. Armstrong holds that the molecules of a metal can unite to form complexes with powers of coherence which vary with the presence of impurity. Crookes by a recent beautiful investigation has taught us how electrical evaporation of solid metals may be set up *in vacuo*, and has shown that even an alloy may be decomposed by such means. We may hope that such work will enable us to understand the principles on which the strength of materials depend.

Before leaving the consideration of questions connected with the molecular constitution of metals, I would specially refer to the excellent work of Heycock and Neville, who have extended to certain metals with low melting-points Raoult's investigations on the effect of impurity on the lowering of the freezing-point of solids. With the aid of one of my own students, H. C. Jenkins, I have further extended the experiments by studying the effect of impurity on the freezing-point of gold. Ramsay, by adopting Raoult's vapour-pressure method, has been led to the conclusion that when in solution in mercury the atom of a metal is, as a rule, identical with its molecule. The important research on the liquation of alloys has been extended by E. Matthey to the platinum gold and palladium gold series, in which the manipulation presented many difficulties ; and E. J. Ball has studied the cases presented by the antimony-copper-lead series. Dr. Alder Wright has continued his own important investigation upon ternary alloys, and A. P. Laurie has worked on the electromotive force of the copper-zinc and copper-tin and gold-tin series, a field of research which promises fruitful results.

In no direction is advance more marked than in the mechanical testing of metals, in which branch of investigation this country, guided by Kirkaldy, undoubtedly took the leading part, and in connection with which Kennedy and Unwin have established world-wide reputations. I would also specially mention the work which has been carried on at the Government testing works at Berlin under Dr. Wedding, and the elaborate investigations conducted at the Watertown Arsenal, Massachusetts, not to mention the numerous continental testing laboratories directed by such men as Bauschinger, Jenny, and Tetmajer. Perhaps the most important recent work is that described by Prof. Martens, of Berlin, on the influence of heat on the strength of iron.

I might have dwelt at length on all these matters without doing half the service to metallurgy that I hope to render by earnestly pleading for the more extended teaching of the subject throughout the country, and for better laboratories, arranged on the model of engineering laboratories, in which the teaching is conducted with the aid of complete, though small " plant" The Science and Art Department has done great and lasting service by directing that metallurgy shall be taught practically, but much remains to be done. With regard to laboratories in works, which are too often mere sheds, placed, say, behind the boiler-house, when may we hope to rival the German chemical firm which has recently spent £19,000 upon its laboratories, in which research will be vigorously conducted ? There is hardly any branch of inorganic chemistry which the metallurgist can afford to neglect, while many branches both of physics and mechanics are of utmost importance to him.

The wide range of study upon which a metallurgical student is rightly expected to enter is leading, it is to be feared, to diminution in the time devoted to analytical chemistry, and this most serious question should be pressed upon the attention of all who are responsible for the training of our future chemists. There can be no question that sufficient importance is not attached to the estimation of "traces," an analysis being considered to be satisfactory if the constituents found add up to 99·9, although a knowledge as to what elements represent the missing 0·1 may be more useful in affording an explanation of the defects in a material than all the rest of the analysis. This matter is of growing interest to practical men, and may explain their marked preference for chemists who have been trained in works, to those who have been educated in a college laboratory.

The necessity for affording public instruction in mining and metallurgy, with a view to the full development of the mineral wealth of a nation, is well known. The issues at stake are so vast that in this country it was considered desirable to provide a centre of instruction in which the teaching of mining and metallurgy should not be left to private enterprise, or even entrusted to a corporation, but should be under the direct control of the Government. With this end in view the Royal School of Mines was founded in 1851, and has supplied a body of well-trained men who have done excellent service for the country and her colonies. The Government has recently taken a step in advance, and has further recognised the national importance of the teaching of mining and metallurgy by directing that the School of Mines shall be incorporated with the Royal College of Science, which is, I believe, destined to lead the scientific education of the nation.

It is to be feared, if the present prices of metals should be maintained, that as regards metalliferous mining, other than that of iron ores, our country has seen its best days, but the extraordinary mineral wealth of our colonies has recently been admirably described by my colleague, Prof. Le Neve Foster, in the inaugural lecture he delivered early in the present year, on his appointment to the chair so long held by Sir Warington Smyth (*Engineering*, vol. li., p. 200 *et seq.*). We shall, however, be able to rightly estimate the value of our birthright when the Imperial Institute is opened next year, and the nation will have reason to be grateful to Sir Frederic Abel for the care he is devoting to the development of this great institution, which will become the visible exponent of the splendours of our Indian and colonial resources, as well as a centre of information.

The rapid growth of technical literature renders it unnecessary for a president of a Section to devote his address to recording the progress of the subject he represents. As regards the most important part of our national metallurgy, this has, moreover, been admirably done by successive presidents of the Iron and Steel Institute, but it may have been expected that references would have been made to the main processes which have been adopted since Percy occupied this chair in 1849. I have not done so, because an enumeration of the processes would have been wholly inadequate, and a description of them impossible in the time at my disposal. Nevertheless it may be well to remind the Section of a few of the more prominent additions the art has received in the last half century, and to offer a few statements to show the magnitude on which operations are conducted. As regards iron, in the last twenty-five years the price of steel has been reduced from £55 per ton to £5 per ton, but, after giving the world the inestimable boon of cheap steel by the labours of Bessemer and of Siemens, we were somewhat slow to accept the teaching of experiment as to the best method of treating the new material : on the other hand, Hadfield has brought manganese steel and aluminium steel within the reach of the manufacturer, and J. Riley has done much to develop the use of nickel steel.

In the case of copper, we have mainly contributed to extraordinary development of wet processes for its extraction from poor sulphides, and have met the great

demands for pure metal by the wide adoption of electrolytic processes.

As regards the precious metals this country is well to the front, for Great Britain and her colonies produce about 38 per cent of the gold supply of the world; and it may be well to add, as an indication of the scale on which operations are conducted, that in London alone 1 ton of gold and 5 tons of silver bullion can easily be refined in a day, No pains have been spared in perfecting the method of assay by which the value of gold and silver is ascertained, and during my twenty years' connection with the Royal Mint I have been responsible for the accuracy of the standard fineness of no less than 555 tons of gold coin, of an aggregate value of £70,500,000 sterling. In the case of the platinum industry, we owe its extraordinary development to the skill and enterprise of successive members of the firm of Johnson, Matthey, and Co., who in later years have based their operations upon the results of the investigations of Deville and Debray. Some indication of the value of the material dealt with may be gathered from the statement that 2¼ cwts. of platinum may easily be melted in a single charge, and that the firm, in one operation, extracted a mass of palladium valued at £30,000 from gold-platinum ore actually worth more than a million sterling.

I wish it were possible to record the services of those who have advanced metallurgy in connection with this Association, but the limitations of time render it difficult to do more than refer to some honoured names of past presidents of this Section. Michael Faraday, president of this Section in 1837 and 1846, prepared the first specimen of nickel-steel, an alloy which seems to have so promising a future, but we may hardly claim him as a metallurgist; nor should I be justified in referring, in connection with metallurgical research, to my own master, Graham, president of this Section in 1839, and again in 1844, were it not that his experiments on the occlusion of gases by metals have proved to be of such extraordinary practical importance in connection with the metallurgy of iron. Sir Lyon Playfair presided over this Section in 1855, and again in 1859. His work in connection with Bunsen, on the composition of blast-furnace gases, was published in the Report of this Association in 1847, and formed the earliest of a group of researches, amongst which those of Sir Lowthian Bell proved to be of so much importance. The latter was president of this Section in 1889. Sir F. Abel, president of this Section in 1877, rendered enduring service to the Government by his elaborate metallurgical investigations, in connection with materials used for guns and projectiles, as well as for defensive purposes. I will conclude this section of the address by a tribute to the memory of Percy. He may be said to have created the English literature of metallurgy, to have enriched it with the records of his own observations, and to have revived the love of our countrymen for metallurgical investigation. His valuable collection of specimens, made while Professor at the Royal School of Mines, is now appropriately lodged at South Kensington, and will form a lasting memorial of his labours as a teacher. He exerted very noteworthy influence in guiding the public to a just appreciation of the labours of scientific men, and he lived to see an entire change in the tone of the public press in this respect. In the year of Percy's presidency over this Section the *Times* gave only one-tenth of a column to a summary of the results of the last day but one of the Meeting, although the usual discourse delivered on the previous evening had been devoted to a question of great importance, "The Application of Iron to Railway Purposes." Space was, however, found for the interesting statement that the "number of Quakeresses who attended the meetings of the Sections was not a little remarkable." Compare the slender record of the *Times* of 1849 with its careful chronicle of the proceedings at any recent meeting of the Association.

In drawing this address to a close, I would point to the great importance of extending the use of the less known metals. Attention is at present concentrated on the production of aluminium, and reference has already been made to the Cowle's process, in which, as in that of Héroult, the reduction of alumina is effected by carbon, at the very high temperature of the electric arc; while, on the other hand, in the Kleiner and similar processes, the electric current acts less as a source of heat than by decomposing a fluid bath, the aluminium being isolated by electrolytic action; and doubtless, in the immediate future, there will be a rapid increase in the number of metallurgical processes that depend on reactions which are set up by submitting chemical systems to electric stress. Incidental reference should be made to the growing importance of sodium, not only in cheapening the production of aluminium, but as a powerful weapon of research. In 1849, when Percy was President of this Section, magnesium was a curiosity; now its production constitutes a considerable industry. We may confidently expect to see barium and calcium produced on a large scale as soon as their utility has been demonstrated by research. Minerals containing molybdenum are not rare; and the metal could probably be produced as cheaply as tin if a use were to be found for it. The quantities of vanadium and thallium which are available are also far from inconsiderable; but we, as yet, know little of the action of any of these metals when alloyed with others which are in daily use. The field for investigation is vast indeed, for it must be remembered that valuable qualities may be conferred on a mass of metal by a very small quantity of another element. The useful qualities imparted to platinum by iridium are well known. A small quantity of tellurium obliterates the crystalline structure of bismuth; but we have lost an ancient art, which enabled brittle antimony to be cast into useful vessels. Two-tenths per cent of zirconium increases the strength of gold enormously, while the some amount of bismuth reduces the tenacity to a very low point. Chromium, cobalt, tungsten, titanium, cadmium, zirconium, and lithium are already well known in the arts, and the valuable properties which metallic chromium and tungsten confer upon steel are beginning to be generally recognised, as the last Exhibition at Paris abundantly showed; but as isolated metals we know but little of them. Is the development of the rarer metals to be left to other countries? Means for the prosecution of research are forthcoming, and a rich reward awaits the labours of chemists who could bring themselves to divert their attention, for even a brief period, from the investigation of organic compounds, in order to raise alloys from the obscurity in which they are at present left.

It must not be forgotten that metallurgical enterprise rests on (1) scientific knowledge, (2) capital, and (3) labour, and that if the results of industrial operations are to prove remunerative much must depend on the relation of these three elements, though it is difficult to determine accurately their relative importance. A modern ironworks may have an army of ten thousand workmen, and commercial success or failure will depend in no small measure on the method adopted in organising the labour. The relations between capital and labour are of so much interest at the present time, that I do not hesitate to offer a few words on the subject.

Many examples might be borrowed from metallurgical enterprises in this and other countries to show that their nature is often precarious, and that failure is easily induced by what appears to be comparatively slight causes. Capitalists might consequently tend to select Government securities for investment in preference to metallurgical works, and the labouring population would then severely suffer. It is only reasonable, therefore, that if capitalists are exposed to great risks, they should, in

the event of success, receive the greater part of the profits. There is a widespread feeling that the interests of capital and labour must be antagonistic, and as it is impossible to ignore the fact that the conflict between them is giving rise to grave apprehension, it becomes the duty of all who possess influence to strive not merely for peace, but to range themselves on the side of justice and humanity. The great labour question cannot be solved except by assuming as a principle that private ownership must be held inviolable, but it must be admitted that there was a time when capital had become arbitrary and some kind of united action on the part of workmen was needed in self-defence. If, however, we turn to the action of the leaders of trade unions in the recent lamentable strikes, we are presented with a picture which many of us can only view as that of tyranny of the most close and oppressive kind, in which individual freedom cannot even be recognised. There are hundreds of owners of works who long to devote themselves to the true welfare of those they employ, but who can do little against the influence of the professional agitator, and are merely saddened by contact with prejudice and ignorance. I believe the view to be correct that some system by which the workman participates in the profits of enterprise will afford the most hope of putting an end to labour disputes, and we are told that profit-sharing tends to destroy the workmen's sense of social exclusion from the capitalistic board, and contents him by elevating him from the precarious position of a hired labourer. No pains should therefore be spared in perfecting a system of profit sharing.

Pensions for long service are great aids to patience and fidelity, and very much may be hoped from the fact that strenuous efforts are being made by men really competent to lead. The report of the Labour Commission which is now sitting will be looked for with keen interest. Watchful care over the health, interests, and instruction of the employed is exercised by many owners of works; and in this respect the Dowlais works, which are being transplanted into your midst at Cardiff, have long presented a noteworthy example. Workmen must not forget that the choice of their own leaders is in their own hands, and on this the future mainly depends. "We may lay it down as a perpetual law that workmen's associations should be so organised and governed as to furnish the best and most suitable means for attaining what is aimed at, that is to say, for helping each individual member to better his condition to the utmost in body, mind, and property." The words will be found in the Encyclical letter which Pope Leo XIII. has recently issued on the "Condition of Labour." To me it is specially interesting that the Bishop of Rome in his forcible appeal again and again cites the opinion of St. Thomas Aquinas, who was a learned chemist as well as a theologian.

Those of us who realise that "the higher mysteries of being, if penetrable at all by human intellect, require other weapons than those of calculation and experiment," should be fully sensible of our individual responsibility. Seeing that the study of the relations between capital and labour involve the consideration of the complex problems of existence, the solution of which is at present hidden from us, we shall feel with Andrew Lang that "where, as matter of science, we know nothing, we can only utter the message of our temperament." My own leads me to hope that the patriotism of the workmen will prevent them from driving our national industries from these shores, and I would ask those to whom the direction of the metallurgical works of this country is confided, to remember that we have to deal both with metals and with men, and have reason to be grateful to all who extend the boundaries, not only of our knowledge, but also of our sympathy.

A Substitute for Cocks in Vacuum Experiments. —F. de Romilly (*Journal de Physique*).—Mercurial joints are used like those in the Töpler-Hagen mercurial air-pump.

ACTION OF LIGHT UPON DYED COLOURS.*

THE primary object of the work of this Committee is to determine accurately the relative fastness to light of all the various colours at present employed by the dyer of textile fabrics. This is to be attained by exposing to direct sunlight and the ordinary atmospheric influences, patterns of silks, wool, and cotton, specially dyed with the various natural and artificial colouring matters.

The work of purifying these colouring matters, dyeing the patterns, recording the dyed and faded colours of each pattern, &c., &c., must necessarily require much time. Moreover, owing to the very large number of colours to be examined, the long exposure needed to give useful results (one year at least), and the limited capacity of the exposing frame employed, the work will naturally proceed but slowly, and will extend over a period of some years.

During the past year the Secretary of the Committee has been engaged in collecting samples of the colouring-matters required for the investigation, and in making preliminary exposure experiments with the view of determining the best method of procedure to be adopted.

Having decided to expose the patterns in groups according to colour, the work of purifying and dyeing with the *red* colouring-matters has been begun, and is now in progress in accordance with a scheme in the hands of members of the Committee.

Of the £20 originally granted to the Committee at the last meeting of the Association in Leeds, the sum of £17 10s. has been expended in the purchase of the necessary silk, wool, and cotton material; also an exposing frame, which has been erected at Adel, in the neighbourhood of Leeds.

Particulars of this expenditure have been forwarded by the Chairman of the Committee to the General Treasurer.

NOTE ON THE
PREPARATION OF BENZENOID DISUBSTITUTED THIOCARBAMIDES FROM PRIMARY AMINES AND CARBON DISULPHIDE.

By EMIL A. WERNER, F.C.S., F.I.C.

WHILE no difficulty is experienced in obtaining an almost theoretical yield of a disubstituted thiocarbamide from a paraffinoid amine and carbon disulphide in what, for all practical purposes, may be called a single operation, the same is not the case when dealing with the benzenoid derivatives. The difference is due to the fact that while the formation of a thiocarbamate, according to the equation—

$$CS_2 + 2NH_2X = CS{<}{NHX \atop SNH_3X} ,$$
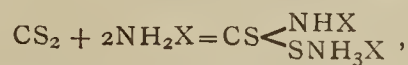
is *complete* after a few moments in the case of the paraffinoid amines, with the benzenoid derivatives a large proportion of the amine remains unchanged, even after several days' standing, and in presence of a considerable excess of carbon disulphide. Indeed, nothing material is gained by using an excess of the disulphide at the outset, but by adopting the following procedure a very high yield of the thiocarbamide may be obtained within a week and with the minimum amount of the disulphide.

The mixture of amine and carbon disulphide in alcoholic solution, after standing over night, is heated on the water-bath, using a vertical condenser until H_2S ceases to be evolved.

The volume of alcohol need not exceed three times that

of the amine used, and purified methylated spirits answers admirably, the thiocarbamide produced being sufficiently pure for most purposes without further crystallisation.

The crop of thiocarbamide which separates on cooling is removed, dried, and weighed, while about one-third of the alcohol is distilled off from the mother-liquor; to this latter a quantity of CS_2 is added, depending on the weight of the thiocarbamide obtained, and considering the remainer of the amine to be free. The mixture after remaining over night is again heated on the water-bath until H_2S ceases to be evolved, &c., &c. This is repeated until five or six crops of the thiocarbamide have been obtained. The preparation is no doubt somewhat tedious, but it requires little attention, and the reward is an almost theoretical yield of the product.

Thus in the course of a recent investigation, necessitating the preparation of some benzenoid thiocarbamide, the yields obtained were as follows:—

1. 64·2 grms. orthotoluidine yielded 69·32 grms. di-orthotolylthiocarbamide = 90·26 per cent of theoretical.

2. 85·6 grms. paratoluidine yielded 96 grms. diparatolyl-thiocarbamide = 93·7 per cent of theoretical.

3. 28 grms. metatoluidine yielded 32·37 grms. of di-metatolylthiocarbamide = 94·90 per cent of theoretical.

4. 72·6 grms. metaxylidine yielded 82·95 grms. of di-metaxylylthiocarbamide = 97·32 per cent of theoretical.

The author's method for the preparation of the benzenoid " mustard oils " (*Journ. Chem. Soc.*, June, 1891), taken in conjunction with the above yields, renders the conversion of an aromatic amine into its corresponding thiocarbimide an operation, which follows closely at the heels of theory.

University Laboratory,
　Trinity College, Dublin.

ABSORPTION - SPECTRUM ANALYSIS OF HIGHLY DILUTE SOLUTIONS.*

By O. KNOBLAUCH.

THE author summarises his results as follows:—

1. Beer's law of absorption (*Poggendorff's Ann.*, ci., p. 248) is valid for the solutions of many salts within a very wide range of concentration. It was found confirmed even when the gaseous pressure corresponding to the proportion of salt in the solution rose from $\frac{1}{3800000}$ atmosphere to 25 atmospheres. The seeming deviations from the law may be traced to physical or chemical changes of the solutions.

2. The differences in the absorption-spectrum of the salts of one metal with different acids or of one acid with different metals remain permanent.

3. The two inferences drawn from the dissociation hypothesis of Prof. Arrhenius on absorption spectra are not found to be confirmed by the observations. In the eosine salts the dilution was so great that 1 grm. of the dissolved body was contained in not less than millions of litres, so that, according to the hypothesis, a complete dissociation of the dissolved molecules must be assumed. According to the second inference, the various eosine salts should have the same absorption-spectrum. This, however, was not the case, but even in dilute solutions the absorption band in the salts of the light metals has a different position from those of the heavy metals. This experimental fact disagrees with the hypothesis.

The two inferences referred to are:—

1. The absorption-spectrum of the concentrated slightly dissociated solution of a body must be different from that of the highly dilute and almost completely dissociated solution; since, in the former, the absorption is produced chiefly by the non-dissociated molecules, but in the latter by the dissociated molecules.

2. At a sufficient dilution at which the limit-condition of dissociation has been reached, the absorption-spectrum of different salts of the same coloured metal (or of the same coloured acid) becomes alike, always supposing that in the dissociated solutions of the salts in question the absorption is produced by the same ion.

CONTRIBUTIONS TO THE CHEMISTRY OF ERBIUM AND DIDYMIUM.*

By GERHARD KRÜSS.

(Concluded from p. 101).

Behaviour of the Earths with Potassium Oxalate (K Brœckelmann and G. Krüss).—A further distinction between the salts of erbium and didymium consists in the behaviour of the oxalates with potassium oxalate. According to Höglund, erbium oxalate behaves with potassium oxalate like the corresponding yttrium salt, which, according to Cleve, dissolves in a hot concentrated solution of potassium oxalate with formation of a soluble double potassium salt. According to the observations of the authors, didymium is not capable of forming such a readily soluble double potassium salt, therefore the following experiment was performed:—

Two hundred grms. didymium and yttrrium nitrates were mixed with the concentrated solution of 1 kilo. potassium oxalate, and digested in heat. The precipitate filtered off after twenty-four hours was dried and ignited. The earth contained in the residue was converted into a neutral nitrate, and showed in its absorption spectrum only a slight indication of the erbium lines, *e. g.*, at $\lambda = 653·9$, and, according to its spectrum, consisted chiefly of didymium and holmium.

The double oxalates which remained in solution, on digestion in potassium oxalate, could not be decomposed by ammonia, whence their solution was first evaporated to dryness with concentrated nitric acid. A micro-crystalline powder was separated out, which, after filtration, solution in much water, precipitation of a voluminous hydroxide with ammonia, and re-solution of the precipitate in nitric acid, yielded a nitrate almost entirely free from didymium.

In order to ascertain whether, besides the erbium earths, colourless earths had passed into the potassium oxalate solution, the molecular weight of the earth thus obtained was determined.

A conversion of oxide into an anhydrous sulphate gave almost the same value as the ignition of a weighed quantity of dry oxalate and its conversion into oxide. As a mean there was formed $\overset{\text{iii}}{R} = 107·1$, whence it follows that in the potassium oxalate solution of the mixed oxalates there was present, along with $\overset{\text{iii}}{Er} = 166$, a considerable quantity of yttrium (atomic weight = about 89), or possibly of scandium.

Some further experiments were made to test the behaviour of mixtures of rare earths with potassium oxalate, and to this end was used an earthy mixture obtained from keilhauite, and not further fractionated. A nitrate solution of such earths was first precipitated with oxalic acid, the oxalates were washed, and boiled for some hours with a concentrated solution of potassium oxalate. A considerable part of the precipitate passed into solution, so that all the lines were present in the absorption spectrum of the solution as in that of the precipitate. If the oxalates are not boiled for some hours with potassium oxalate, but digested only at the common temperature of a room, an erbium passes into solution, the absorption spectrum of which shows no trace of the Diγ lines at $\lambda = 579·2$ and 575·4.

The following experiment proves that along with erbium, in addition to yttrium, other colourless earths pass into solution on the digestion of the oxalate with potassium oxalate. The concentrated solution of potassium salt, with which the oxalates were digested for some hours, was evaporated to dryness, the residue ignited and extracted with water. Besides the potassium carbonate obtained a part of the earths was now soluble in water, for the solution yielded a precipitate with ammonia.

The hydroxide, after being well washed, yielded a nitrate solution, which in its most concentrated state, and in a stratum of several centimetres in thickness, showed only one line, *i. e.*, Erβ at λ = 523·1. The line was faint, so that along with a little erbium a colourless earth was chiefly present in the nitrate in question. To obtain a decision a determination of the molecular weight was undertaken. To this end the earth present was most carefully purified, small portions of the metals precipitable by hydrogen sulphide being first removed from the solution of the nitrate. The filtrate of the precipitate was boiled and precipitated with ammonia, the hydroxide thrown down was dissolved in nitric acid, the earth was again precipitated with oxalic acid from an acid solution, and the oxalate was converted by ignition into an oxide almost perfectly white ; its colour was very slightly altered on ignition in a current of hydrogen, and it consisted of a colourless earth accompanied by traces of erbia and perhaps also of didymia.

On analysis it was found that 0·2166 grm. of the oxide yielded 0·4727 grm. of anhydrous sulphate, showing a $\overset{\text{III}}{R} = 77·5$. The small quantity of colourless earth obtained in this simple manner from keilhauite consists therefore chiefly of scandia, since only the presence of this oxide can reduce the atomic weight below the value of yttrium. By a treatment of the earthy oxalates with potassium oxalate it is therefore possible, by a single operation, to eliminate erbium, and many colourless earths, from didymium, and under the above experimental conditions quickly to obtain a scandium material.

Behaviour of the Neutral Solution of the Nitrates of the Rare Earths with Alcohol (K. Bröckelmann).—Concerning a differing solubility of the earthy nitrates in alcohol there have been hitherto no definite communications. It must therefore be remarked that the neutral nitrate solution of the (nearly) colourless earth obtained by the potassium oxalate process as just described, and having the low atomic weight ($\overset{\text{III}}{R} = 77·5$), can be completely precipitated by the addition of an excess of alcohol. This is the more striking as an ordinary nitric solution of the rare earths — *e. g.*, such as they are directly obtained from the gadolinites—is not precipitable by alcohol.

Further experiments were therefore made, in the first place with a didymium material obtained by the methods above described, and having the mean atomic weight. This didymium could not be resolved into portions having different spectra, either by fractionated crystallisation or by the decomposition of the nitrates by heat.

The faintly acid solution of this didymium was evaporated to dryness on the water-bath, and taken up in a little water, so as to obtain a neutral solution of nitrate as concentrated as possible. This liquid was mixed with a large excess of absolute alcohol, the whitish precipitate was filtered off and washed with alcohol. The nitrates insoluble in alcohol were dissolved in a little water, again precipitated with alcohol, and this treatment was repeated three times. A portion each time passed into solution, and the earth obtained after this thrice-repeated alcoholic precipitation as an insoluble nitrate was submitted to several determinations of its molecular weight.

The earth possesses the properties of didymium oxide of being reducible in a current of hydrogen to a lower oxide. The oxide was light brown, the sub-oxide white: 0·4521 grm. oxide yielded on ignition 0·4491 grm. sub-

oxide, which corresponds to a decrease of oxygen of 0·66 per cent. Hence it was seen that it was not a didymium in the ordinary sense of the word (Cleve's and Brauner's didymium), for those *savants* found a greater difference in the percentage of oxygen in the two stages of oxidation of didymium. The same holds good with cerium. It was also evident, from the relatively faint absorption-spectrum of the nitrates precipitable by alcohol, that we have in these precipitates a mixture of colourless earth with such as produce absorption spectra, and that therefore, by treating the nitrates with alcohol, one more colourless earth could be removed from ordinary didymium.

In order to obtain a clue to the nature of this earth, the nitrates insoluble in alcohol were dissolved in water, carefully purified for determination, converted into oxalate oxide, and then, by ignition in a current of hydrogen, into sub-oxide. Weighed quantities were converted into anhydrous sulphate, and on the analysis of different products the following results were obtained :—

Grammes of Suboxide taken.	Grammes of Anhydrous Sulphate found.	Atomic Weight calculated for a $\overset{\text{III}}{R}$.
0·2342	0·4417	111·4
0·0861	0·1625	111·9
0·2594	0·4928	111·5
	Mean	111·6

The values obtained were considerably lower than the mean atomic weight of didymium : 144—145.

Hence, especially as the spectroscopic examination pointed to a mixture of didymium with a colourless earth obtained by treating the ordinary didymium nitrate with alcohol, yttrium and perhaps also scandium have been removed from the didymium. Further, the material insoluble in alcohol was purified by frequently repeated treatment of the neutral nitrate with alcohol. The thrice precipitated material with the above mean atomic weight of 111·6, after a fourth similar treatment, showed almost the same atomic weight, $\overset{\text{III}}{R} = 111·28$.

Still the above behaviour of the didymium nitrate is interesting, and should be taken into account in the preparation of pure didymium material. It should be examined whether, on treating the concentrated neutral solution of nitrate with alcohol, an earth of lower atomic weight may not be separated from didymium oxide.

The above research on the elements of the yttrium and cerium group affords some contributions towards the mutual separation of these elements from each other. It is at the same time evident, from the experiments cited, how sparingly characteristic are the properties of the several rare earths from an analytical point of view, and that difficulties have to be encountered in the separation of these oxides. It is therefore questionable whether many of the rare elements actually possess the atomic weights which have been hitherto attributed to them. In a succeeding memoir the observations made in this respect upon erbium will be communicated.

ON THE DETERMINATION OF NITRATES IN WATER.*

By ALLEN HAZEN and HARRY W. CLARK.

I. *Phenosulphonic Acid Process.*

THE accurate determination of nitrates, in large numbers of samples of water, has presented considerable difficulty. A few years ago the phenolsulphonic acid process (Grandval and Lajoux, *C. R.*, July 6, 1885) was selected, as being on the whole the most satisfactory, and with it we have made several thousand determinations.

The process consists, essentially, of evaporating a measured portion of water to dryness, and treating the residue with a solution of phenol in sulphuric acid, a portion of which the nitric acid liberated converts into nitrophenols, which, when made alkaline, are strongly yellow. The colour so produced is compared with that obtained in a similar way from known quantities of potassium nitrate.

The accuracy of the results was greatly increased by adding sodium carbonate to prevent the loss of nitric acid during evaporation, and by decolourising yellow surface waters by alumina.

The best results were obtained with about 1 c.c. of a 5 per cent solution of strictly pure phenol in sulphuric acid nearly free from water, added to the dry residue, and without warming. Caustic soda or potash was substituted for ammonia, in neutralisation, to avoid the fumes of the latter.

An attempt was made to use standards made from pure picric acid, but to our surprise their colour was only a third as deep as that of standards made by treating potassium nitrate with phenolsulphonic acid. Other nitrophenols were then tried, but none matched the standards perfectly. It was possible to match particular standards by mixing different nitro-compounds, but for other standards different mixtures were required. It was obvious that in our standards, prepared from potassium nitrate, we were not dealing with a pure compound, but with a mixture of varying proportions of different nitrophenols, and, as the different compounds are by no means of the same colour for equal contents of nitrogen, variations in the proportions of the different compounds formed gave rise to very serious errors. The principal products are usually ortho- and para-mononitrophenol in varying proportions.

The following table shows the strength of solutions of some of the nitrophenols which give colours equal to those of average standards prepared from potassium nitrate, when seen through a depth of 8 inches of solution :—

Comparison of Solutions of Netrophenols.

(Parts per Million Nitrogen in a Depth of 8 Inches.)

Standard from KNO₃.	Orthomono-Nitrophenol.	Paramono-Nitrophenol.	Dinitrophenol.	Trinitrophenol.
0·02	0·022	0·014	0·04	0·06
0·04	0·040	0·026	0·08	0·14
0·06	0·060	0·044	0·12	0·22
0·08	0·076	0·064	0·18	0·32
0·10	0·090	0·08	0·23	0·42
0·12	0·110	0·12	0·31	0·60
0·14	0·124	0·16	0·38	0·80
0·20	0·16	0·36	0·60	1·40
0·40	0·22	1·80	1·40	3·00
0·60	0·30	7·00	3·00	6·00
1·00	0·38	12·00	6·00	9·00
1·40	0·46		9·00	
4·00	1·00			
10·00	2·00			

We have not been successful in so controlling the reaction as to get a constant product, or in finding a substituted phenol with which there can be only a single nitro-compound, and which is at the same time sufficiently soluble in water, and otherwise adapted to the process. If such a compound could be found the accuracy of the process might be greatly increased.

The presence of chlorine lowers the result, often seriously. The error increases with the ratio of chlorine to nitrate, but is not proportional to it. Numerous experiments do not show sufficient regularity to allow even an approximate estimate of the error in particular cases. The results of this process upon a hundred and fifty ground waters averaged 11 per cent lower than the results obtained by reduction by the aluminum process, with the precautions to be described, and it is believed that this represents approximately the average error due to chlorine in these particular cases. In some instances we have removed the chlorine with silver sulphate, and obtained higher results; but even then the results are liable to the errors described above.

This process, with proper precautions, gives results usually too low, and often much too low, and, while it may be useful in some cases, we have been unable to obtain results of the desired accuracy.

(To be continued).

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JULY 31ST, 1891.

By WILLIAM CROOKES, F.R.S.;

WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford;

and C. MEYMOTT TIDY, M.B., F.C.S., Barrister-at-Law, Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, Metropolis Water Act, 1871.

London, August 5th, 1891.

SIR,—We submit herewith the results of our analyses of the 186 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from July 1st to July 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 186 samples examined, the whole were found to be clear, bright, and efficiently filtered.

The character of the water supply to the Metropolis during the month of July was in all respects satisfactory, the proportion of organic matter present in the water being below even the exceptionally small amount recorded in the month of May.

There was not found to be any appreciable difference in character between the water distributed by the five Companies taking their supply from the Thames, and the water distributed by the East London Company, who take their supply from the Lea; but what slight difference was found to exist was in favour of the Lea-derived water, as shown in the following Table :—

	Ratio of brown to blue tint.	Oxygen required for oxidation.	Organic carbon per 100,000	Organic carbon per 100,000
	Means.	Means.	Means.	Maxima.
Thames supply :—				
January				
February				
March	13·0 : 20	0·051	0·147	0·209
April				
May	9·6 : 20	0·042	0·136	0·150
July	8·9 : 20	0·046	0·121	0·142
Lea supply :—				
July	8·2 : 20	0·041	0·119	0·124

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
WILLIAM ODLING.
C. MEYMOTT TIDY.

CONTRIBUTIONS TO MICRO-CHEMICAL ANALYSIS.*

By H. BEHRENS.

(Continued from p. 112).

XXIII.—*Gold.*

1. STANNOUS chloride produces in the solution of gold a red turbidity which is very well suited for microscopical recognition. It is best to place the specimen and the reagent near each other, and allow the drops to flow together. There then appears a rather sharply marked red streak at the point of contact. The limit of the reaction is 0·002 m.grm. Au.

2. Thallous sulphate produces in solutions which contain at least 0·17 gold the crystallisation of long, yellow needles of thallous aurochloride. The needles may exceed the length of 1000 micro. The limit of the reaction is 0·01 m.grm. Au.

The solution is concentrated by evaporation as far as possible, partly in order to expel nitric acid, and a granule of thallous sulphate is introduced into the drop when cold. The reaction sets in at once and is localised around the reagent. The application of heat readily occasions a reduction of gold, and the separation of hexagonal leaflets of thallic chloride.

3. Ammonium sulphocyanide produces in solution of gold a red powdery precipitate, which, in an excess of the reagent, is converted into pale red, woolly rosettes. A larger excess dissolves if heated to a colourless liquid, which precipitates salts of zinc and cobalt in a manner similar to ammonium-mercuric sulphocyanide. Zinc-gold sulphocyanide is lemon-yellow, cobalt-gold sulphocyanide a blue green. Their form agrees with the form of the corresponding double salts of mercuric sulphocyanide. Together they form sea-green mixed crystals. It is not yet certain whether there may be formed mixed crystals containing mercury and gold.

XXIV.—*Platinum.*

(a) *Platinous Chloride.*—1. Precipitation as cprammonium-chloroplatinite (salt of Millon and Commaille). If a solution of potassium chloroplatinite is mixed with a little copper sulphate, rather much sal-ammoniac, and an excess of ammonia, violet needles are quickly deposited, which, in solutions with 0·1 per cent potassium chloroplatinite become 200 micro. in length, and are deposited in a recognisable form when they contain 0·01 per cent. Limit of the reaction 0·00006 m.grm. Pt.

(b) *Platinic Chloride.*—1. Potassium chloride yields well-developed yellow octahedra of 10—50 micro. In solutions containing less than 0·1 per cent platinum chloride, potassium chloride acts too slowly; very dilute solutions must be evaporated to dryness in order to obtain crystals of potassium-platinum chloride. If alkaline salts are present in considerable quantity, this process is not satisfactory, and we are compelled to have recourse to the reactions 2 or 3. Limit of the reaction with potassium chloride 0·0006 m.grm. Pt.

2. Rubidium chloride precipitates almost instantaneouly solutions containing 0·1 per cent of platinum chloride. The crystals of rubidium chloroplatinate are about one-third of the size of those of the potassium salt.

Cæsium chloride reacts instantaneously in solutions containing 0·03 per cent of platinum chloride. The crystals have then a diameter of 2 micro. Limit of the reaction 0·0002 m.grm. Pt.

3. Thallous sulphate reacts distinctly with platinic chloride diluted to 1·20,000. The crystals are very small, and from concentrated solutions there is precipitated a yellow dust. Confusion with chloroiridiate is excluded, as iridic chloride is reduced by thallous sulphate. The limit of the reaction is 0·000004 m.grm. Pt.

* *Zeit. Anal. Chemie.*

XXV.—*Palladium.*

1. Potassium iodide throws down a brown, flocculent precipitate, which dissolves with a reddish brown colour in an excess of the reagent.

With ammonia palladio-iodide gives orange-red needles and a colourless solution, from which palladammonium iodide is deposited in pale yellow, rectangular rosettes of 20—30 micro. An excess of potassium iodide interferes. As a corrective evaporation with hydrochloric acid may be tried. Limit of the reaction 0·0001 m.grm. Pd.

2. Ammonium sulphocyanide produces a brown colouration in solutions of palladium. An addition of thallous sulphate then produces a strong, yellowish brown precipitate, the solution of which in hot water deposits rectangular rosettes of 100 micro. which grow to iridescent leaflets. From very dilute solutions there are obtained rectangular prisms and crosses of 30 micro. The reaction is still produced when the palladium nitrate is diluted with 5000 parts of water. Its limit is at 0·00007 m.grm. Pd.

XXVI.—*Iridium.*

1. Rubidium chloride instantly precipitates a solution of iridium sal-ammoniac (ammonium chloriridiate) in 300 parts of water; in a solution with 1500 parts of water there appears in some minutes a vermilion-red precipitate consisting of octahedra of 10 micro.

Cæsium chloride throws down at the same dilution almost instantly very small but well-developed red octahedra. The limit of the reaction is 0·0003 m.grm. Ir.

XXVII.—*Rhodium.*

1. Potassium nitrite throws down from acid and ammoniacal solutions of rhodium yellow cubes of 2—4 micro. The precipitate adheres to the glass like potassium-cobalt nitrite. The liquid may be diluted with 10,000 parts of water. The limit lies at 0·00009 m.grm. R.

XXVIII.—*Ruthenium.*

1. Cæsium chloride produces in solutions of ruthenium in aqua regia a reddish brown, finely granular precipitate, soluble in hot water, but being re-deposited unchanged from this solution. Limit of reaction 0·0008 m.grm. Ru.

2. Potassium sulphocyanide colours acid ruthenium solutions a violet-red. If the colour does not appear at once the liquid is concentrated by a gentle heat, and the margin of the specimen drop is carefully watched. The reaction is not sensitive; its limit is 0·0012 m.grm. Ru. It is useless in presence of iron, cobalt, platinum, and palladium. A good micro-chemical reaction for ruthenium has yet to be discovered.

XXIX.—*Osmium.*

1. Cæsium chloride produces in solutions of osmic acid in hydrochloric acid a whitish precipitate consisting of greenish yellow octahedra of 10—30 micro. The limit of the reaction is 0·0001 m.grm. Os.

2. Ammonium chloride, added in excess to solutions of potassium osmite, separates yellow rods (40—70 micro.), and dendrites of osmiotetrammonium-dichloride. The limit of the reaction is 0·0005 m.grm. Os.

In less dilute solutions the reduction to potassium osmite (with potassa-lye and potassium nitrite or alcohol) yields characteristic crystals of osmite—

$$K_2OsO_4 + 2H_2O,$$
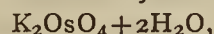
which separates out in fine, violet-red octahedra, of 50 micro.

XXX.—*Tin.*

(a) *Stannous Chloride.*—Gold chloride produces in solutions containing stannous chloride a flocculent red precipitate, or in very dilute solutions a red turbidity. (See Gold 1). Limit of the reaction 0·00007 m.grm. Sn.

2. Mercuric chloride is reduced by stannous salts to insoluble mercuric chloride, even in very dilute solutions. (Compare Mercury *b* 2). Limit 0·00007 m.grm. Sn.

3. Oxalic acid is recommended by Haushofer as a reagent for stannous salts. The use of potassium oxalate increases the sensitiveness, which, however, is far below 1 and 2. The crystals are mostly imperfect, H-shaped, and polarise strongly. Limit of the reaction 0·001 m.grm. Sn.

In all these reactions it must be remembered that arsenic acid forms with tin a very stable, insoluble compound, which is not readily decomposed by hydrochloric acid.

(*b*) *Stannic Chloride.*—1. Cæsium chloride precipitates from solutions of stannic chloride colourless octahedra of Cs_2SnCl_6. (Compare Cæsium 1). The precipitation is but little interfered with by hydrochloric acid. An addition of potassium iodide slightly increases the sensitiveness and colours the crystals yellow. The limit of this convenient and trustworthy reaction is 0·00045 m.grm. Sn.

2. The changes of form which stannic chloride occasions in the oxalates of barium and strontium have been mentioned under Strontium 4. In acid liquids the greatest sensitiveness is reached with strontium salts. Limit of the reaction 0·0002 m.grm. Sn.

Meta-stannic acid must be fused with alkali or reduced with magnesium. It is dissolved in hydrocloric acid and treated in the first case according to *b* 1, in the second according to *a* 1 or 2.

XXXI.—*Titanium.*

1. Potassium salts precipitate from solutions of titanium dioxide in hydrofluoric acid, potassium fluotitanate, in pale rectangular figures, rhombs, octagons, and long hexagons of 60—90 micro. The precipitation is tedious, and the limit is 0·06 m.grm. Ti.

If rutile is fused with potassium fluoride at a bright red heat, and the melt is dissolved in hot water, needles are deposited which might be taken for fluotantalate. They dissolve in hydrochloric acid, and the solution yields the tabular crystals just mentioned.

2. Rubidium chloride precipitates fluoriferous solutions of titanic acid more readily than potassium chloride. Solutions containing 0·2 per cent of titanium dioxide give within 2 minutes crystals of rubidium fluotitanate. They measure 15—40 micro., and otherwise resemble those of the potassium salt. Cæsium chloride instantly precipitates tablets of 8—12 micro. Limit of the reaction 0·001 m.grm. Ti.

Insoluble titanic acid may be fused with alkali, the melt extracted with hot water, and the residue dissolved by heating with concentrated hydrochloric acid. It is preferable to fuse with sodium fluoride and dissolve the melt in dilute hydrochloric acid.

XXXII.—*Zirconium.*

1. Potassium bioxalate precipitates from solutions of zirconium sulphate (down to a proportion of 0·01 per cent of the sulphate) colourless pyramids of 20—60 micro. (probably tetragonal), similar to strontium oxalate, but more readily soluble in hydrochloric acid. The limit of the reaction is 0·00006 m.grm. Zr.

Oxalic acid gives a precipitate only when diluted down to 200 parts. Titanium solutions are not precipitated by oxalic acid and bioxalates; neutral oxalate precipitates small rods. Zircon is best opened up by means of sodium fluoride like titanium, and evaporating down with sulphuric acid.

2. Rubidium chloride occasions in solutions of zirconium sulphate or chloride, mixed with hydrochloric acid and ammonium fluoride, a separation of colourless octahedra, which measure 30—60 micro. The rubidium chloride yields the same strongly refractive crystals in the hydrochloric solution of a melt of zircon and sodium fluoride. Cæsium chloride gives similar, though smaller, crystals. The limit of the reaction is 0·0005 m.grm. Zr.

XXXIII.—*Thorium.*

1. Heating to close upon 100°, precipitates from solutions of thorium sulphate, if not too dilute, fine needles of 70—100 micro. of the sparingly soluble salt with 3 mols. of water. The limit of the reaction is 0·03 m.grm. Th.

Upon one end of the port-object is laid a covering-glass, upon which is laid the specimen drop. It is heated to incipient ebullition, the marginal crust is broken, and the covering-glass is pushed upon the cold half of the port-object. This is a rapid and trustworthy reaction for quantities of thorium which are not too minute. Confusion with the sulphates of the cerite metals (especially lanthanum) and the needles of gypsum remains excluded if we test further with ammonia and with ammonium carbonate (see 3).

2. Oxalic acid produces a white powdery precipitate, sparingly soluble in hydrochloric acid, more readily soluble in ammonia and ammonium carbonate. Very dilute solutions yield a finely crystalline oxalate, especially rods of 4 micro. The limit of the reaction is 0·0001 m.grm. Th.

3. Thallous sulphate occasions in ammoniacal solutions of thorium the separation of sharp colourless rhombs and flat rhombic pyramids of 30—40 micro. Very dilute solutions yield during evaporation along the margin rhombs of 4—10 micro. The limit of the reaction is 0·00005 m.grm. Th.

The solution to be examined is precipitated with ammonium carbonate, adding an excess, and the solution is accelerated by adding ammonia. A granule of thallous sulphate sets up the reaction above mentioned. From uranium thorium is distinguished by reactions 1 and 2.

(To be continued).

NOTICES OF BOOKS.

Water Works' Statistics, 1891. Edited by C. W. HASTINGS. London: Hazell, Watson, and Viney.

THE usefulness of this compilation is still somewhat limited by the neglect or refusal of local bodies to supply information. The town of Aylesbury still maintains silence, though it has assuredly no reason to be ashamed of its water-supply. Stafford, Stowmarket, and Stockport likewise vouchsafe no information as far as we can trace, but many towns whose names begin with R and S are, by some accident, placed in unalphabetical order.

The heading " Source of Supply " is still open to amendment. Ambleside sensibly says that its water comes from the " green slate," whilst Bacup gives as its source " sandstone and peat." But, on the other hand, some towns say merely that they derive their water from " wells," or from " gathering grounds," without any clue to the character of the formation. A few places still assign " gravitation " as the source of their supply, leaving its origin an open question.

The information concerning the quality of the water is often lacking in precision. Many towns call their water simply " good," " soft," or " hard," as the case may be, whilst others give the degree of hardness. The local death rates are omitted in a number of cases. We can find little definite relation between the mortality of the towns and the character of the water-supply as hard or soft. So many other factors, however, intervene in determining the death rate of a town, that the omission is of the less importance.

The statistics of the water-supplies in Scotland, Wales, and Ireland are given very promiscuously, and mixed up with such localities as Shanghai, St. Petersburg, and Monte Video.

The daily consumption per head is a feature of no little importance both to sanitarians and to all persons interested in the utilisation of sewage. But a very large proportion of towns have vouchsafed no information.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

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Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxiii., No. 6, August 10, 1891.

This issue does not contain any chemical matter.

Vol. cxiii., No. 7, August 17, 1891.

A New Blowpipe for Mineral Oils.—M. Paquelin. —This apparatus comprises three essential parts : a blow-pipe—properly speaking—a carburettor, and a double-action blast. The blowpipe is formed of a single tube, like the mouth blowpipe used by jewellers. The jet has this characteristic, that it emits two kinds of flames : a central flame with a very narrow point, and small lateral flames in the form of petals. The curburettor serves for three purposes : (1) to mix air and the vapours of the oil in proportions regulated at will ; (2) to exhaust the combustible of all its useful elements ; and (3) to regulate the length of the flame at pleasure. These results are obtained by means of two cocks and a saturator. One of the cocks is of a special structure ; the other is of the ordinary make.

New Researches on the Solar Atmosphere.—H. Deslandres.—The author has studied the atmosphere of the sun in a part of its radiation not yet explored. He has obtained the permanent feeble ray, rather more refrangible than H, and indicated in Young's list with the note " element unknown." He has identified this ray with a hydrogen ray. In the invisible ultra-violet portion he has recognised two new permanent rays which correspond to the two first rays of hydrogen of the stellar series of Dr. Huggins. The most striking result is the marked predominance of the rays attributed to calcium ; the corresponding rays rise *higher* than hydrogen, which contradicts our received ideas on the composition of the solar atmosphere.

Mechanical Determination of the Catenation of the Atoms of Carbon in Organic Compounds.—G. Hinrichs.—The atoms of carbon do not as generally represented follow a single right line.

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Bulletin de la Société Chimique de Paris.
Series 3, Vol. v., No. 11.

On the Second Principle of Thermodynamics and its Application to Chemical Phenomena. — H. Le Chatelier.—To render Carnot's principle applicable to chemical phenomena it is merely necessary to suppress every restriction on the nature of the equilibrium, the re-establishment of which is in question, which is tantamount to striking out the term " caloric " in Carnot's enunciation. We then read, " Wherever there may be re-establishment of equilibrium there may be production of motive power, and reciprocally wherever such power is consumed it is possible to occasion a breach of equilibrium." This leads us, without calculation, to two chemical laws which have long been known—the *law of the triple point* and the *law of the maximum stability* of the various states of a body. From the same principle there may be deduced by a very simple calculation the two laws of *iso-dissociation* and of the direction of chemical movement. The same method of calculation is applicable to the quantity of available energy furnished by the return of a chemical system towards its state of equilibrium.

On the Allotropic Transformations of Metals.—H. Le Chatelier.—From the author's experiments it results that metals, as regards their molecular transformation, behave exactly like the other bodies studied in chemistry —that is, the transformations either take place abruptly,

the metal behaving in that case like all crystalline bodies (definite compounds or isomorphous mixtures), or progressively in the case of alloys which behave like amorphous mixtures (solutions or glasses). The existence of these two states in metals is shown in many cases by a simple inspection of the fracture. The extreme variability of the mechanical properties of metals is explained without the intervention of any special isomerism by remarking that they depend not only on the chemical state of the metal, but on the form and the dimensions of the crystals or granules of metal which are in juxtaposition, and on the manner of distribution of the impurities.

On Some Combinations of Pyridine.—Raoul Varet. —An account of the preparation and properties of pyridine bromocadmiate, bromozincate, bromonickelate, bromocuprate, iodocuprite, cyanocuprite, cyanomercurate, cyano-argentate, argentoiodide, argentobromide, and argentochloride.

Formation of Dimethylacrylic Acid in the Preparation of the Amido-Acids of Isovaleric Acid.—E. Duvillier.—The relatively small product of amido-acids obtained on causing ammonia and the compound ammonias to react upon bromoisovaleric acid, is due to the simultaneous formation of a notable quantity of dimethylacrylic acid.

Researches on the Influence of Wines upon Pepsic Digestion.—L. Hugounenq.—Without dwelling upon the known action of alcohol, which has been well studied by Petit, and upon that of cream of tartar, the novel results arrived at in the author's researches are the following :—1. All wines, without exception, interfere with the action of pepsine—those richest in alcohol, cream of tartar, and colouring-matter being most injurious, as it was easy to foresee. 2. Among the elements of natural wine the colouring-matters act in concert with the alcohol and the cream of tartar to retard or arrest pepsic digestion. 3. The acidity of normal wines is unable to excite the action of pepsine ; in most cases it does not appear to assist. 4. Among the colouring-matters introduced fraudulently into wines, methylene blue, azoflavine, solid blue, and especially magenta, interfere with pepsic digestion. The vegetable colours, black mallows, elderberries, and maki, like œnoline exert an injurious action. 5. Plastering, by removing a part of the cream of tartar, eliminates an element of natural wines which retards the action of pepsine *in vitro*. Digestion is more rapid in presence of plastered wines than of natural wines, but the advantage which plastered wines have in this respect does not conceal their other disadvantages.

On the Use of Metaphenylenediamine to Detect Active Oxygen.—P. Cazeneuve.—The author makes a solution of 1 per cent of the hydrochlorate of this base in alcohol at 93 per cent. Ten drops of ammonia are added to the solution. If this reagent is exposed to the air, or exposed to a current of oxygen for many hours, it takes a slightly greenish blue tint. A few drops of oxygenated water added to 10 c.c. of the reagent colour it intensely blue in a few minutes in the cold.

On a Violet Colouring-Matter Derived from Morphine. On the Formula of Pseudomorphine.—P. Cazeneuve.—The author has caused paranitrosodimethylaniline to react upon morphine. He obtains a violet colouring-matter which is neither an indophenol nor a safranine, but which may enter the group of the azines or the indamines, or constitute the type of a special group of colouring-matters. The pure colouring-matter has the composition $N{<}^{C_6H_4 \cdot N(CH_3)_2}_{C_{17}H_{19}NO_4}$. It is amorphous, with a bronze reflection. It is to a certain extent soluble in water, from which it is precipitated by common salt. It is very soluble in methylic, ethylic, and amylic alcohols, in which it displays very decided dichroism. In amylic alcohol especially it is red by reflected light, and violet by transmitted light. The aqueous solution, if poured upon

strong sulphuric acid, gives, like the safranines, a green zone, then blue, and then violet. It dyes wool, silk, and gun-cotton in a direct manner. The shade produced on silk is brilliant, but it does not withstand light. This morphine violet is the first true colouring-matter obtained from a natural alkaloid.

On the Hydrazonic Derivatives of β-Naphtho-quinone.—E. Noelting and E. Grandmougin.—The colouring-matters derived from the hydrazone of β-naphthoquinone, and especially its sulphonic derivative, which is an isomer of the oranges I. and II. of commerce, have all the characters of the azo-compounds. Their study leads the authors to conclude that the hydrazone of β-naphthoquinone is an azo-derivative, and not a hydrazone. This sulphonic derivative is a true ponceau, which is quite distinct from the oranges I. and II. No hydrazone hitherto obtained has been a red dye, even the dihydrazones, the osazones being at most oranges. The authors describe the phenylhydrazone of β-naphtho-quinone; orthophenylazo-α-naphthol; the transformation of β-benzeneazo-α-naphthol (hydrazone of β-naphtho-quinone) into benzenedisazo-α-naphthol; the acetyldisazo-α-naphthol; and the ethylic and methylic ethers of disazo-α-naphthol.

On Certain Orthoxyazo-Derivatives of α-Naphthol and Hydrazones of β-Naphthoquinone.—E. Noelting and E. Grandmougin.—The authors describe certain orthoxyazo-derivatives of α-naphthol, which they have prepared in order to compare them with the para-azo-derivatives of α-naphthol. They are red colours, true ponceaus, whilst their isomers of the para series are browns, more or less inclining to yellow.

A Transposition on the Formation of the Diazo-Derivatives of α-Naphthol. — E. Noelting and E. Grandmougin.—The authors wish to compare the products obtained by the action of diazobenzol chloride upon the hydrazines of β-naphthoquinone, derived from sulphanilic hydrazine, and the hydrazine of metamidobenzoic acid with those formed by the action of diazotised sulphanilic and metamidobenzoic acid upon phenylazo-α-naphthol. The products were not identical as it might have been expected.

Action of Fluorine upon Phosphorus Trifluoride.—Henri Moissan.—If acted on by fluorine, phosphorus trifluoride passes at once into the pentafluoride. The reaction is attended with flame, like that of chlorine on phosphorus trichloride.

The Place of Fluorine in the Classification of the Simple Bodies.—Henri Moissan.—The author places fluorine at the head of the halogen family. There is, however, a difference in the respective behaviour of fluorine and chlorine with other elements. When fluorine combines with non-metals it forms compounds more volatile than the corresponding chlorides. When it unites with metals it yields products whose melting-point is higher than that of the corresponding chlorides. Calcium fluoride seems to approximate to calcium oxide more than to the chloride. Silver fluoride is very soluble in water, whilst the chloride is insoluble. Aluminium chloride is decomposed by water, whilst aluminium fluoride is insoluble and very stable. The fluoric ethers have always a higher boiling-point than the corresponding chlorine compounds; they are very stable, and less easily saponified. The action of fluorine upon the organic hydrogen compounds is so violent that no intermediate compounds are produced. Fluorine decomposes water in the cold, yielding ozone of such a concentration that it appears with the fine blue colour indicated by Hautefeuille and Chappuis.

TO CORRESPONDENTS.

B. L.—Aqua fortis is the commercial name for nitric acid.

THE CHEMICAL NEWS.

ADDRESS TO STUDENTS.

IN attempting to give anything in the shape of advice to students we are too generally met with the reply, " *Non possumus !* " If we exhort them to qualify themselves for extending the boundaries of any of the sciences, and for solving some of the difficult problems which each presents to us—in a word for research, instead of cramming for examinations—we are told that this is, in reality, advice to immolate themselves for the honour of their country and for the benefit of mankind. If we bid them give their attention to chemistry and physics, rather than to " classics," we find that in too many cases they have no option.

Schools and colleges are still organised on what might be called the mediæval type. Principals, masters, tutors of all grades, are selected from the ranks of those whom Mr. Arnold calls " the poor humanists," and who naturally give prominence to those studies in which they have themselves been exclusively trained. A few days ago there fell into our hands the prospectus of a day-school for boys on the Limited Liability principle. Its vice-presidents and its council consist largely of D.D.'s, Rev. M.A.'s, &c.; but there is in the list not a single D.Sc., Ph.D., or M.D. Nor do we recognise in the list the name of any man who has made his mark in the scientific world. The curriculum certainly includes " elementary science." But it is placed down towards the bottom of the list along with such disciplines as singing and shorthand. We fear that the amount of time and attention which it will receive will be very subordinate, and utterly out of proportion to its importance.

Now if a youth is educated at such establishments what chance has he for devoting his attention mainly to Science ?

There is another way in which scientific studies are heavily handicapped by dint of the examination system. When a certain number of marks is required to gain some distinction, or when a position is open to the candidate who obtains the highest number, the total number to be gained by the utmost proficiency in the physical and natural sciences is fixed most unfairly low. What shall we say of an examination in which the maximum possible in organic chemistry was 250, whilst Greek and Latin might earn 400 each ? What wonder if experienced " coaches " tell the student that science does not " pay," and that young men renounce their prospects of a brilliant reputation in the hope, instead, of earning scholarships, fellowships, and other tangible rewards of " passing." In the face of such conditions what boots the advice given by ourselves, as well as by men of higher standing ? Charm we never so wisely, we address ears deafened by the instinct of self-preservation. Hence we find ourselves placed in a vicious circle, from which the student—especially the individual student—has little power of escaping. We should recommend him, however, wherever possible, to give his countenance and his sympathy to the friends of Mr. Auberon Herbert, and to throw all the cold water at his disposal upon the examination system, its advocates, and its organs.

It is incumbent on every student of Science to earn freedom for himself and for those who may succeed him. The Jesuits, it will be remembered, first imported examinationism from its native China and acclimatised it in Europe. But even they did not bind down the pupils to one Procrustean curriculum, but they gave free course to different tastes and different capacities.

UNIVERSITIES AND COLLEGES.

UNIVERSITY OF LONDON.

CANDIDATES for any Degree in this University must have passed the Matriculation Examination. No exemption from this rule is allowed on account of Degrees obtained or Examinations passed at any other University. This and all other Examinations of the University, together with the Prizes, Exhibitions, Scholarships, and Medals depending upon them, are open to Women upon exactly the same conditions as to Men.

There are two Examinations for Matriculation in each year ; one commencing on the second Monday in January, and the other on the second Monday in June.

The Examination is conducted by means of Printed Papers ; but the Examiners are not precluded from putting, for the purpose of ascertaining the competence of the candidates to pass, *viva voce* questions to any candidate in the subjects in which they are appointed to examine. These Examinations may be held not only at the University of London, but also, under special arrangement, in other parts of the United Kingdom, or in the Colonies.

Every candidate for the Matriculation Examination must, not less than five weeks before the commencement of the Examination, apply to the Registrar for a Form of Entry, which must be returned not less than four weeks before the commencement of the Examination, accompanied by a Certificate showing that the candidate has completed his sixteenth year, and by his Fee for the Examination. As no candidate can be admitted after the List is closed, any candidate who may not have received a Form of Entry within a week after applying for it must communicate immediately with the Registrar, stating the exact date of his application and the place where it was posted.

Every candidate entering for the Matriculation Examination for the first time must pay a Fee of Two pounds to the Registrar. If a candidate withdraws his name, or fails to present himself at the Examination, or fails to pass it, the Fee shall not be returned to him, but he shall be allowed to enter for any subsequent Matriculation Examination upon payment, at every such entry, of an additional Fee of one pound, provided that he comply with the Regulations in the preceding paragraph.

Candidates are not approved by the Examiners unless they have shown a competent knowledge in each of the following subjects :—Latin. Any one of the following Languages : — Greek, French, German, Sanskrit, or Arabic. The English Language, and English History, with the Geography relating thereto. Mathematics. Mechanics. One of the following branches of Experimental Science :—Chemistry, Heat and Light, Magnetism and Electricity, Botany.

The Examination in Chemistry is—Chemistry of the Non-metallic Elements ; including their compounds, their chief physical and chemical characters, their preparation, and their characteristic tests.

A Pass Certificate, signed by the Registrar, will be delivered to each candidate after the Report of the Examiners has been approved by the Senate.

If in the opinion of the Examiners any candidates in

the Honours Division of not more than twenty years of age at the commencement of the Examination possess sufficient merit, the first six among such candidates will receive an Exhibition of thirty pounds per annum for the next two years; the second among such candidates will receive an Exhibition of twenty pounds per annum for the next two years; and the third will receive an Exhibition of fifteen pounds per annum for the next two years; such exhibitions are payable in quarterly instalments provided that on receiving each instalment the Exhibitioner declares his intention of presenting himself either at the two Examinations for B.A., or at the two Examinations for B.Sc., or at the Intermediate Examination in Laws, or at the Preliminary Scientific M.B. Examination, and Intermediate Examination in Medicine, within three academical years from the time of his passing the Matriculation Examination.

Under the same circumstances, the fourth among such Candidates will receive a prize to the value of ten pounds in books, philosophical instruments, or money; and the fifth and sixth will each receive a prize to the value of five pounds in books, philosophical instruments, or money.

Any candidate who may obtain a place in the Honours Division at the Matriculation Examination in January is admissible to the Intermediate Examination either in Arts or in Science in the following July.

INTERMEDIATE EXAMINATION IN SCIENCE.

The Intermediate Examination in Science will be held July 18, 1892.

No candidate (with the exception of such as have obtained Honours at the Matriculation Examination in the preceding January) is admitted to this Examination within one academical year of the time of his passing the Matriculation Examination.

The Fee for this Examination is £5.

Examination for Honours.

Candidates for Honours in Chemistry will be examined in Inorganic Chemistry, treated more fully than in the Pass Examination. In addition, they will be examined practically in Simple Qualitative Analysis. This Examination will consist of six hours' examination by two printed papers and of six hours' practical work.

In the Examination for Honours, the Candidate, not being more than 22 years of age at the commencement of the Pass Examination, who most distinguishes himself will receive an Exhibition of £40 per annum for the next two years.

B.Sc. EXAMINATION.

The B.Sc. Examination will be held October 17, 1892.

Candidates for this Examination are required to have passed the Intermediate Examination in Science at least one academical year previously.

The Fee for this Examination is £5.

Examination for Honours.

The examination for Honours in Chemistry will take place on Monday and Tuesday in the week following the Examination for Honours in Mathematics; on Monday by printed papers (chiefly on Organic Chemistry), and on Tuesday by practical examination in Qualitative and Quantitative Analysis.

The candidate, being not more than 23 years of age, who most distinguishes himself in Chemistry, will receive £50 per annum for the next two years, with the style of University Scholar.

DOCTOR OF SCIENCE.

The examination for the Degree of Doctor of Science takes place annually within the first twenty-one days of June.

No candidate is admitted to the examination for the Degree of D.Sc. until after the expiration of two Academical Years from the time of his obtaining the Degree of B.Sc. in this University.

Every candidate for this Degree must state in writing the special subject within the purview of the Faculty of Science, as set out in the Programme of the B.Sc. Ex-

amination, upon a knowledge of which he rests his qualification for the Doctorate; and with this statement he shall transmit an original printed Dissertation or Thesis (at least six copies) treating scientifically some special department of the subject so named, embodying the result of independent research, or showing evidence of his own work, whether based on the discovery of new facts observed by himself, or of new relations of facts observed by others, or, generally, tending to the advancement of Science. The Dissertation or Thesis shall have been written in view of candidature, or shall have been published within the two academical years immediately preceding. Every candidate may further specify any printed contribution or contributions to the advancement of Science which he has at any time previously published, and every contribution so specified and submitted shall be considered and taken as part of his qualification for the Degree. If the Dissertation or Thesis be approved by the Examiners, the candidate shall be required to present himself at the University upon such day or days within the first twenty-one days of June as may be notified to him, and shall, at the discretion of the Examiners, be further tested, either orally or practically, or by printed questions or by all of these methods, and with especial reference to his Dissertation or Thesis.

Candidates for the Degree of D.Sc. will be expected to be so fully conversant with the branch of Science they profess as to be able, if required, to satisfy any test of their acquirements in that branch that it may be thought expedient to apply.

The Fee for this Examination is £10.

In October, 1892, modifications of these Regulations will come into operation, particulars of which can be obtained of the Registrar.

PRELIMINARY SCIENTIFIC (M.B.) EXAMINATION.[*]

This Examination takes place twice in each year,—once, for Pass and Honours, commencing on the third Monday in July; and once for Pass Candidates only, commencing on the third Monday in January.

No candidate shall be admitted to this Examination unless he shall have passed the Matriculation Examination. Not less than five weeks before the commencement of the Examination he must apply to the Registrar for a Form of Entry, which must be returned not less than four weeks before the Examination, accompanied with the candidate's fee.

The Fee for this examination is Five Pounds.

EXAMINATION IN SUBJECTS RELATING TO PUBLIC HEALTH.

A Special Examination will be held in December in subjects relating to public health.

No candidate is admitted to this Examination unless he has passed the Second Examination for the Degree of Bachelor of Medicine in this University at least one year previously; nor unless he shall have given notice of his intention to the Registrar at least two calendar months before the commencement of the Examination.

The Fee for this Examination is £5.

UNIVERSITY OF OXFORD.

Waynflete Professor of Chemistry.—W. Odling, M.A., F.R.S.

Every Student must reside in one or other of the Colleges or Halls, or in licensed lodgings, for a period of three years, passing at least two examinations in Arts, and one in either Mathematics, Natural Science, Law, Modern History, or Theology, when, if he obtain a first, second, or third class, he can take his B.A. Degree; if he do not gain such honour he has to pass a third examination in *Literis Humanioribus.*

The fee for students working in the Laboratory for three days in the week during the Term is £3; for students working every day, £5.

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[*] Candidates who pass in all the subjects of the Preliminary Scientific (M.B.) Examination, and also pass *at the same time* in the Pure and Mixed Mathematics of the Intermediate Examination in Science, or who have previously passed the Intermediate Examination in Arts, are admissible to the B.Sc. Examination.

Scholarships of about the value of £75 are obtainable at Christ Church, Magdalen, and other colleges, by competitive examination in Natural Science.

More detailed information may be obtained from the University Calendar; from the professors; and from the Sub-Librarian in the Radcliffe Library or the Museum.

UNIVERSITY OF CAMBRIDGE.

Professor of Chemistry.—G. D. Liveing, M.A., F.R.S.

Jacksonian Professor of Natural and Experimental Philosophy.—J. Dewar, M.A., F.R.S.

The Student must enter at one of the Colleges or Hostels, or as a Non-collegiate Student, and keep terms for three years by residence in the University. He must pass the previous examination in Classics and Mathematics, which may be done in the first or third term of residence, or, through the Oxford and Cambridge Schools Examination Board, or through the Senior Local Examinations, before commencing residence. He may then proceed to take a Degree in Arts, either continuing mathematical and classical study, and passing the ordinary examinations for B.A., or going out in one of the Honour Triposes.

The scholarships, ranging in value from £20 to £10 a year, are chiefly given for mathematical and classical proficiency. Scholarships are given for Natural Science in Trinity, St. John's, St. Peter's, Clare, Christ's, Sidney, Pembroke, Caius, Downing, and Cavendish Colleges; the examinations being in December, at Easter, and in June and October.

The Chemical Laboratory of the University is open daily for the use of the Students. The Demonstrators attend daily to give instructions. A list of the lectures is published annually, in June, in a special number of the *Cambridge University Reporter*, which may be had from the Cambridge Warehouse, in Paternoster Row, or through any bookseller.

Non-collegiate Students are allowed to attend certain of the College Lectures and all the Professors' Lectures, and have the same University status and privileges as the other Students. Full particulars may be obtained by forwarding a stamped directed envelope to the Assistant Registrar, Cambridge, or from the *Cambridge University Calendar.*

UNIVERSITY OF DUBLIN.
TRINITY COLLEGE.

Professor of Chemistry.—J. Emerson Reynolds, D.Sc., M.D., F.R.S., V.P.C.S.

Assistant Lecturer.—Emil A. Werner, F.C.S., F.I.C.

Demonstrator.—William Early, F.I.C.

The general Laboratories include working accommodation for 120 Students, and the Quantitative and Research Laboratories for about 40 Students. The Laboratories will open on the 1st of October. Lectures will commence about November 1st.

The Laboratories and the Lectures of the Professor of Chemistry can now be attended by Students who do not desire to reside in the University or proceed to its Degrees.

The full Course of General and Analytical Chemistry occupies three years, but a Student is free in his third year to devote most of his time to a special department of Pure or Technical Chemistry. Students can enter for any portion of the Course. The following Lectures are delivered:—

1. *Inorganic Chemistry and Chemical Philosophy.*— Elementary, first year; advanced, second year.
2. *Organic Chemistry.* — General, second year; advanced, third year.
3. *Metallurgy.*—A Course for Engineering and Technical Students.

The Laboratories are open every day from 10 to 5 o'clock (except Saturdays, when they close at 1 o'clock).

The Summer Course of Practical Chemistry for Medical Students begins during the first week in April and terminates with the first week in July.

The University of Dublin grants the Degree of Doctor of Science to graduates of Master's standing whose independent researches in any branch of Science are of sufficient merit.

KING'S COLLEGE.
(DEPARTMENT OF ENGINEERING AND APPLIED SCIENCE).

Professor of Chemistry.—J. M. Thomson, F.C.S.

Demonstrator of Practical Chemistry.—G. S. Johnson, F.C.S.

Assistant Demonstrator.—Herbert Jackson, F.C.S.

On Tuesday and Friday at 10.20 a.m. Students of the First Year are admitted to the Course of Theoretical and Applied Chemistry. The Course commences with a View of the Forces which concur to the production of Chemical Phenomena, after which the laws of Chemical Attraction are discussed, and the Non-metallic elements and their principal Compounds are described.

The Metals and their principal compounds are next examined, care being taken to point out the applications of the Science to the Arts; and the processes of the different Manufactures and of Domestic Economy are explained and illustrated.

Examinations of the Class, both *vivâ voce* and by written papers, are held at intervals during the course at the usual Lecture hour.

Second Year.—Students attend in the Laboratory twice a week, on Tuesday and Friday, at 10.20, and they go through a course of Manipulation in the most important operations of Chemistry, including the first steps of Analysis.

Any Student of this Department may be admitted to this Class at any period of his study on payment of an extra fee.

Experimental and Analytical Chemistry in the Laboratory.—The object of this Class is to afford to Students who are desirous of acquiring a knowledge of analysis, or of prosecuting original research, an opportunity of doing so under the superintendence of the Professor and Demonstrator; Students may enter, upon payment of extra Fees, at any time except during the vacation, and for a period of one, three, six, or nine months, as may best suit their convenience. The laboratory hours are from ten till four daily, except Saturday, on which day the hours are from ten till one.

In addition to the Laboratory Fee, each Student defrays the expenses of his own Experiments. The amount of this expense, which is comparatively trifling, is entirely under his own control.

Special hours and fees are arranged for the convenience of such Third Year Students as wish to study Analytical Chemistry.

Fees.—Chemistry per term, £3 3s. 0d.; per ann., £8 8s. 0d.; Practical Chemistry per term, £4 4s. 0d.; per ann., £10 10s. 0d.; Experimental and Analytical Chemistry—One Month (daily attendance), £4 4s. 0d.; Three Months (daily attendance), £10 10s. 0d.; Six Months (daily attendance), £18 18s. 0d.; Nine Months (daily attendance), £26 5s. 0d. A student taking a month's ticket may attend daily during 1 month, or 3 days a week during 2 months, or 2 days a week during 3 months.

Rules as to Admission of Students.

I. The Academical Year consists of Three terms: Michaelmas Term, from beginning of October to the week before Christmas; Lent Term, from the middle of January to the week before Easter; Easter Term, from Easter to the beginning of July.

II. The days fixed for the Admission of New Students in the Academical Year 1891-92, are Tuesday, September 29, Wednesday, January 13, and Wednesday, April 27.

METALLURGY.

Professor.—A. K. Huntington, F.I.C., F.C.S., &c.

The following subjects are treated of in the Lectures: The Selection and Economic Preparation of Fuel and of Refractory Materials; the methods by which metals are obtained from their ores, and the means by which they are rendered suitable for the various requirements of the Arts.

Particular attention is made to the study of the Nature and Properties of Metals and Alloys available for Constructive Purposes.

In the Metallurgical Laboratory, which is always open during College hours, the relation between the Chemical Composition of Metals and their Mechanical Properties may be studied by the aid of Testing Machinery. The instruction given to each student is regulated by his special requirements.

PHOTOGRAPHY.

Lecturer.—J. M. Thomson, F.R.S.E., F.C.S.

Arrangements are made for a complete Course of Instruction in Photography to the students of the third year. A glass house has been erected, and in connection with it a Laboratory for the preparation of Photographic Chemicals. Students entering to this department will be afforded every facility for practising the Art in all its branches.

In addition to the regular College Course in Photography occasional classes are formed, consisting each of about six gentlemen, who meet twice a week. The fee for private instruction is £5 5s. for ten lessons, or £10 10s. for three courses. There is in every case a charge of £1 each course for chemicals.

EVENING CLASSES.

Classes for Evening Instruction in various subjects are held during the months from October to March, inclusive, and during the months of April, May, and June.

UNIVERSITY COLLEGE.
FACULTY OF SCIENCE.

Professor.—William Ramsay, Ph.D., F.R.S.

Assistant Professors.—R. T. Plimpton, Ph.D., and J. N. Collie, Ph.D.

Assistants.—C. F. Baker, B.Sc., and P. B. Williams.

The Session is divided into three Terms, as follows, all the dates being inclusive :—

First Term, from Friday, October 2nd, until Friday, December 18th;

Second Term, from Tuesday, January 5th, 1892, till Friday, April 1st;

Third Term, for Lectures, from Tuesday, April 26th, till Friday, July 1st. Class Examinations occupy about ten days, beginning on Monday, June 20th.

Junior or Matriculation Course.

Tuesday, Thursday, and Saturday, at 10, commencing October 7, 1891, and April 14th, 1892. Fee :—£4 4s.

These Courses will each consist of about thirty lessons, partly theoretical and partly practical, on the non-metallic elements. Frequent exercises will be given.

Senior Course of Chemistry.

First and Second Terms : Inorganic.—The Class meets four times a week: Mondays, Wednesdays, Fridays, and Saturdays, at 9, for Lectures, Examinations, and Exercises, commencing October 6th.

Fee :—For the Course, £7 7s.; Perpetual, £9 9s.; for the First or Second Terms, £4 4s.

This Course and the Practical Class cover the subject as prescribed for the Preliminary Scientific (M.B.) and Intermediate Examination in Science of the University of London.

For the Preliminary Scientific Examination Students who take the three subjects for that examination in July attend during the First and Second Terms.

Advanced Course of Chemistry.

Second and Third Terms.—The class meets twice a week, on Tuesdays and Thursdays, at 9. The hour will be altered by special arrangement with the class if necessary.

Fee :—For the Course, £3 3s.; for a Term, £2 2s.

This Course will be found suitable for those about to proceed to graduation as Bachelor of Science in London University, and to those who intend to choose Chemistry as a profession. Such students should also work in the Laboratory during as many hours as they can spare.

Organic Chemistry.

Tuesday and Thursday, at 9, in the First Term; Tuesday, Thursday, and Saturday, at 10, in the Second Term ; and Tuesday and Thursday, at 9, and Saturday, at 11, in the Third Term. The hour of meeting will be altered should the class desire it.

This Course of Organic Chemistry is intended for those who in studying the subject have not a Medical Examination chiefly in view. Candidates for Honours at the Int. M.B. are, however, recommended to attend this Course during the Second and Third Terms, instead of the Special Summer Course.

The Course includes the subjects required at the B.Sc. Examination, Pass and Honours; but no previous acquaintance with Organic Chemistry will be expected of those joining the Class.

Fee :—For the Course, £6 6s.; for a Term, £2 12s. 6d.

An Advanced Course for those engaged in prosecuting research in Organic Chemistry will be held three times a week during the Second Term. Fee, £2 12s. 6d.

Practical Class.

First and Second Terms, Tuesday and Thursday, at 11, commencing October 7th.

Fee, including cost of materials, £5 5s.; for a Second Course, £3 3s.

The Course includes the Practical Chemistry required at the Preliminary Scientific and Intermediate Science Examinations.

Senior Practical Class.

Wednesdays from 2 to 4 and Saturdays from 10 to 12 during the Third Term.

Fee :—(Including cost of materials) £5 5s.; for a Second Course, £3 3s.

Analytical and Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4 p.m., Saturdays excepted, from October until the middle of July, with a short recess at Christmas and at Easter.

Fees: for the Session, £26 5s.; six months, £18 18s.; three months, £10 10s.; one month, £4 4s.

Three specified days a week :—for the Session, £15 15s.; six months, £11 11s.; three months, £6 6s.; one month, £2 12s. 6d., exclusive of expense of materials. Students may enter at any period of the Session.

The Laboratory Course includes the Practical Chemistry required at the following Examinations of the University of London :—Prel. Sci. (M.B.), Intermediate M.B., Intermediate Science, B.Sc.

Students who wish to attend the Lectures on Chemical Technology may acquire here the requisite preliminary knowledge of Practical Chemistry and Analysis.

When accompanied by, or preceded by, attendance on the Lectures on Inorganic and Organic Chemistry, the Laboratory Course qualifies Students in the application of Chemistry to Manufactures, Metallurgy, Medicine, or Agriculture, &c.

There is also a Chemical Library containing the chief Journals and Standard Works on Chemistry.

A Gold Medal and Certificates of Honour are competed for by first year's Students. The Tuffnell Scholarship (£100 for two years) will also be competed for in the Session 1891-92; also the Clothworker's Scholarship of £30.

Chemical Technology.

Lecturer, Watson Smith, F.I.C., F.C.S.

Courses of Lectures will be given on the following subjects:—Manufacture of Sulphuric Acid, Alkali, &c. Fuel and Gas Manufacture. Chemical Technology of Building Materials. Coal tar Products and Colours. Applications of Chemistry to Engineering. Construction of Chemical Plant.

Evening Lectures will be given by gentlemen qualified by practical and theoretical acquaintance with special subjects, and occasional visits to Works will be arranged.

Residence for Students.

Students can obtain residence at University Hall,

Gordon Square. Particulars can be obtained at the office of the College.

ROYAL COLLEGE OF SCIENCE AND ROYAL SCHOOL OF MINES.

Professor.—T. E. Thorpe, Ph.D., B.Sc., F.R.S.
Assistant Professor.—W. P. Wynne, B.Sc., A.R.C.S.
Demonstrators.—H. Chapman Jones and A. E. Tutton.
Assistants.—G. S. Newth, J. W. Rodger, and W. Tate.

The Royal College of Science at South Kensington is intended, primarily, for the instruction of teachers, and of students of the industrial classes selected by competition in the examinations of the Science and Art Department. The Royal School of Mines is incorporated with the Royal College of Science. Students entering for the Associateship of the School of Mines obtain their general scientific training in the Royal College of Science. The instruction in the Royal College of Science is arranged in such a manner as to give the Students a thorough training in the general principles of Science, followed by advanced instruction in one or more special branches of Science. The Associateship is granted in certain divisions or lines of study. Students who go through any one of the prescribed courses of instruction and pass the necessary Examinations receive a Certificate of Associateship of the Royal College of Science, or of the Royal School of Mines. But students who are not candidates for the Associateship are permitted to take up the course of instruction in one or more special branches of science, and on passing the examination receive a Certificate to that effect. The Associateship of the Royal College of Science is given in one or more of the following divisions :—Mechanics, Physics, Chemistry, Biology, Geology, and Agriculture, and the Associateship of the Royal School of Mines in Metallurgy and Mining.

The course of instruction, which lasts for three years, is the same for all the divisions during the first year, after which it is specialised in accordance with the Scheme detailed in the Prospectus of the School.

The Session is divided into two Terms. The first Term begins on the 30th of September and ends about the middle of February. The second Term begins in the middle of February and ends about the middle of June.

Examinations are held at the end of each course of instruction and at such other periods as may be found necessary. On the results of these examinations the successful candidates are arranged in two classes, first and second. There are also " Honours " examinations for the subjects of the third year, the successful candidate being placed in order of merit. A student obtains the Associateship who passes in all the subjects of the first two years and in those of the special division he selects for his Associateship. A student who goes through the prescribed course of instruction in any subject and passes the final examination in it receives a certificate to that effect.

Students who do not wish to attend the lectures are admitted for short periods to the laboratories, at the discretion of the Professors. The fees for the laboratories are £4 per month.

Students not entering for the Associateship are admitted to any particular course of study, so far as there is room, on payment of the fees shown in the following table :—

	Lectures. £	Laboratory. £
Chemistry	3	13
Physics	5	12
Biology with Botany	5	12
Geology with Mineralogy ..	4	8
Mechanics	4	6
Metallurgy	4	13
Mining	4	
Agriculture	4	10
Astronomical Physics	2	

Mathematics and Mechanical Drawing, £3 per term. Geometrical Drawing £3 per session. Freehand Drawing, £1 per term.

The fees for the first two years amount to about £75, and for the remainder of the course for the Associateship they vary from £30 to about £40.

Both the private and the State-aided students are required to furnish themselves with certain instruments and apparatus before the commencement of the courses. These are enumerated in the syllabuses of the several subjects.

Officers of the Army, Navy, and Civil Service, recommended by their respective Departments, are admitted to the Lectures and Laboratories at half the foregoing charges.

Associates of the Royal College of Science or of the Royal School of Mines have the privilege of free admission to the Library and to all the courses of lectures.

Bona fide teachers qualified to earn payments for teaching Science according to the rule of the Science Directory may attend any course of lectures on the payment of £1.

Several valuable Exhibitions, Scholarships, and Prizes are attached to the studentship.

Summer Courses for Teachers.—Short courses of instruction are given annually, about July, in different branches of science for the benefit of teachers of science schools in the country. The courses last three weeks. About 200 teachers are admitted to them, and they receive 3rd class railway fare to and from South Kensington and a bonus towards their incidental expenses of £3 each. (See Science Directory.)

Working Men's Lectures.—Notification of these will be given in the newspapers.

THE SCHOOL OF PHARMACY
OF THE
PHARMACEUTICAL SOCIETY OF GREAT BRITAIN.

The Fiftieth Session will commence on Thursday, October 1st, 1891. Entries not previously arranged with the Dean may be made between 10 a.m. and 5 p.m. on that day.

Officers of the School :—Prof. Attfield, Ph.D., F.R.S., F.I.C., Practical Chemistry ; Prof. Dunstan, M.A., F.I.C., Chemistry ; Prof. Green, M.A., B.Sc., F.L.S., Botany ; Mr. Joseph Ince, F.L.S., Pharmacy and Practical Pharmacy ; Mr. Henry George Greenish, F.I.C., F.L.S., Materia Medica.

Dean of the School, Prof. Attfield, F.R.S.

Entries may be made for single classes. A bench in the chemical laboratories can be engaged at any time for any number of hours daily or days weekly for any period. Students are recommended to join the Lecture classes on Chemistry and Physics in October, but other convenient periods are the beginning of January or the commencement of the Second Course in April. Certificates of attendance at the two Courses of Lectures on Chemistry and at the Chemical Laboratories are accepted as evidence of chemical training by the Institute of Chemistry in connection with the Examinations for the Associateship, and also by the conjoint Board of the Royal Colleges of Physicians and Surgeons, as well as by other examining bodies. Certificates of attendance on the Courses of Pharmacy also are accepted by the conjoint Board.

For Prospectuses, &c., apply to either of the Officers, or to the Dean, Prof. Attfield, F.R.S., at the School, 17, Bloomsbury Square, London, W.C.

UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH.

Professor.—H. Ll. Snape, D.Sc. (Lond.), Ph.D. (Gœttingen), F.I.C.
Demonstrator.—A. W. Warrington, M.Sc. (Vic.)., F.I.C.

The College is open to male and female students above the age of sixteen years. The Session commences on Monday, September 27, on which day all Students will be expected to meet the Professors in the Library of the College.

Lecture Courses.—(1) Matriculation Course; two lectures weekly during the Lent and three during the Easter Term. (2) Intermediate Science Pass Course; three lectures weekly during the Lent and Easter Terms. For those Students who have selected Physics or Botany instead of Chemistry at the Matriculation Examination, an Introductory Course of three lectures weekly will be delivered during the Michaelmas Term. (3) Intermediate Science Honours Course; two lectures weekly during the Lent and Easter Terms. (4 and 5) B.Sc. Pass and Honours Courses; each three lectures weekly throughout the Session.

Laboratory Courses.—The Laboratory is open daily from 10 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays. Classes for the Systematic Study of Qualitative and Quantitative Analysis will be formed, and Special Courses will be arranged for those who intend to follow Medicine or Pharmacy, or any one particular branch of Applied Chemistry, always provided that such Students possess the requisite knowledge of Theoretical Chemistry. The hours will be arranged to suit the requirements of the individual Student.

Students intending to proceed to the M.B. or B.Sc. Degree of the University of Edinburgh may count one or two years' residence respectively spent at this College.

Fees.—The Fee for the whole Session, if paid in advance, is £10; if paid by Single Terms, for the first term of attendance in each Session, £4; for the second term, £3 10s.; for the third term, £3. These composition fees enable the Student to attend any or all the Classes of the College, with the exception that a small extra fee is charged for Laboratory Instruction. Thus, for Practical Chemistry, the additional fee is, for six hours' work per week, 10s. per term, and for twelve hours, 20s. per term. The fees for those who desire to spend several days weekly in the laboratory may be learned on application to the Registrar. Fee for a single Lecture Course £1 per term.

Scholarships and Exhibitions varying in value from £10 to £40 per annum will be offered for competition at examinations which commence on September 15, and exhibitions are awarded at the end of the Session on the results of the class examinations.

The Chemical Laboratories in connection with this College have been recently built, and are fitted with every convenience for the prosecution of chemical studies.

UNIVERSITY COLLEGE OF NORTH WALES, BANGOR.

Chemistry.—Professor, James J. Dobbie, M.A., D.Sc. Demonstrator, George McGowan, Ph.D., F.R.S.E. Assistant Lecturer in Agricultural Chemistry, F. C. Archibald.

Physics.—Professor, Andrew Gray, M.A., F.R.S.E. Demonstrator, David M. Lewis, M.A.

The Session opens September 30th, 1890. All regular classes are open to men and women students above the age of 16 years. The following Courses of Lectures will be given.

Matriculation Course.—Subjects: Those prescribed for the London University Matriculation Examination. Fee for the Term £2 2s. A class for revision of Matriculation Work will be held during the Summer Term. Fee for the Term, £1 1s.

Intermediate Course. — Inorganic Chemistry and Elementary Physical Chemistry. Fee for the Term £2 2s.

B.Sc. Course.—Organic Chemistry. Fee for the Session, £3 3s.

Medical Course.—Inorganic and Organic Chemistry. Fee for the whole Course, £4 4s.

Agricultural Chemistry.—Fee, £1 1s.

Laboratory Courses.—The laboratory is open on five days of the week from 10 a.m. to 4 p.m. for instruction in Chemical Analysis and in the Application of Chemistry to Medicine and the Industrial Arts. Fees: six hours

per week, £1 1s. per Term; twelve hours, £2 2s.; eighteen hours, £3 3s.; twenty-four hours, £4 4s.

A Committee has been appointed to frame a complete scheme of Agricultural Instruction for North Wales, and the College has received a grant of £500 from the Board of Agriculture. Three Dairy Schools in connection with the College have been established in Welshpool, Denbigh, and Bangor, and an Agricultural Department is now open, in which students may receive a complete training in Agricultural Science.

UNIVERSITY COLLEGE OF SOUTH WALES AND MONMOUTHSHIRE.

Professor.—C. M. Thompson, M.A., D.Sc., F.C.S.
Demonstrator.—G. S. Turpin, M.A., D.Sc., F.C.S.

The Session commences October 5th, and terminates on June 24th, and is divided into three terms.

The Junior Course (delivered during the Michaelmas term only) consists of about 55 lectures, and will cover the subjects prescribed for the London University Matriculation examination. Fee, £2 2s. A revision class is held in the Summer term.

The Intermediate Course consists of 90 lectures in continuation of the Junior Course, and, together with laboratory practice, will cover the subjects required for the Intermediate Examination in Science and the Prel. Sci. (M.B) Examination of the University of London. Fee £3 3s.

The Senior Course includes some 90 lectures devoted to Organic Chemistry; Fee, £3 3s.

An Elementary Organic Course of 10 lectures, and a course of 30 lectures on Qualitative and Quantitative Analysis will also be given.

In the laboratory each student works independently, so that the course of study may be adapted to the requirements of the individual. Hours, 9 to 1 and 2 to 4.30; Saturday, 9 to 1. Fees—Six hours per week, £3 3s. per session; twelve hours, £2 2s. per term; eighteen hours, £3 3s. per term; twenty-four hours £4 4s. per term.

Professors Thompson and Parker are recognised by the Universities of Edinburgh, Glasgow, and Aberdeen as teachers in Chemistry and Natural History respectively, so that registered Medical Students can spend one year of their course at the University College, Cardiff. The College is also recognised as an institution at which two years of the course for the degree of Bachelor of Science of the University of Edinburgh may be spent.

Students by making a payment of £10 at the commencement of each session may compound for all lecture fees for the whole session. Laboratory fees are not included in the composition fee, but Students preparing for the Science Examinations of the University of London or the Medical Courses at the Universities of Edinburgh, Glasgow, and Aberdeen, may, by making a payment of £13 13s. at the commencement of each Session, compound for both Lecture and Laboratory Fees during the Session.

At the entrance examination in September, and the annual examination in June, several scholarships and exhibitions are awarded. Great importance is attached to special excellence in one subject.

The College Prospectus, and also further information as to scholarships, may be obtained from the Registrar.

A Hall of Residence for Female Students is attached to the College.

UNIVERSITY COLLEGE, BRISTOL.

Professor of Chemistry.—Sydney Young, D.Sc.
Lecturer.—Arthur Richardson, Ph.D.

The session 1891-92 will begin on October 8th. Lectures and classes are held every day and evening throughout the Session. In the Chemical Department lectures and classes are given in all branches of theoretical chemistry, and instruction in practical chemistry is given daily in the chemical laboratory. The department of experimental physics includes various courses of lectures arranged progressively, and practical instruction is given in the physical

and electrical laboratory. The Department of Engineering and the Constructive Professions is designed to afford a thorough scientific education to students intending to become engineers, or to enter any of the allied professions, and to supplement the ordinary professional training by systematic technical teaching. This department includes courses specially arranged for students intending to become civil, mechanical, electrical, or mining engineers, surveyors, or architects. Those who attend the mechanical engineering course enter engineering works during the six summer months, and, in accordance with this scheme, various manufacturing engineers in the neighbourhood have consented to receive students of the College into their offices and workshops as articled pupils at reduced terms. Medical education is provided by the Bristol Medical School, which is affiliated to the College. Several Scholarships are tenable at the College. Full information may be obtained of the Secretary.

Day Lectures.

Inorganic Chemistry.

The Course treats of the principles of Chemistry, and of the Chemistry of the Non-Metals and Metals.

Lectures will be given daily at 9 and 11 o'clock.

Organic Chemistry.

This Course will relate to the more important groups of the Compounds of Carbon.

Lectures will be given during the Second Term on Tuesdays and Thursdays at 10 o'clock; during the Third Term on Mondays, Wednesdays, and Fridays at 10 o'clock. Fee, £3 3s.

Practical Chemistry.—Laboratory Instruction.

The Laboratory will be open daily from 10 a.m. to 5 p.m., except on Saturdays, when it is closed. Instruction will be given in the Laboratory in all branches of Practical Chemistry, including Qualitative and Quantitative Inorganic and Organic Analysis, the preparation of Chemical Products, and Inorganic and Organic Research. Special facilities will be afforded to those who desire to study Practical Chemistry as applied to the different processes employed in the Arts and Manufactures, and to Scouring, Bleaching, and Dyeing. The Laboratory is under the immediate supervision of the Professor and the Lecturer. Fees in Guineas—

	5 Days a Week.	4 Days a Week.	3 Days a Week.	2 Days a Week.	1 Day a Week.
Per Session	15	13	10	7½	5
„ Two Terms ..	11	9	7½	5½	4
„ One Term ..	6	5	4	3	2
„ Month	3	2½	2	1½	—

Students may arrange to divide their days of laboratory work into half-days.

Analytical Course.

A Course of Lectures on the Principles of Qualitative Analysis will be given during the First and Second Terms; it is intended to supplement the instruction in Practical Chemistry. All first year's Laboratory Students are expected to attend this Course. The Lectures will be given on Mondays at 10 a.m. Fee, £1 1s. for the two Terms.

Photographic Chemistry.

Special arrangements can be made with regard to instruction in this subject.

Chemical Scholarship.—Among others, a Chemical Scholarship of £25 is offered for competition.

Evening Lectures.

Two courses of Lectures will be delivered during the First and Second Terms; they will be devoted to the consideration of the general Principles of Chemistry and Chemical Physics and the Chemistry of Non-Metallic Elements. Special attention will be paid throughout to those products which have a practical application in the Arts and Manufactures. Fee for each course, 7s. 6d.

University College, Bristol, has been approved by the Council of the Institute of Chemistry as a College at which all the subjects required for the admission of Associates to the Institute are taught, and as a centre for the Practical Examination.

MASON SCIENCE COLLEGE, BIRMINGHAM.

Professor.—W. A. Tilden, D.Sc. Lond., F.R.S.

Assistant Lecturers.—W. W. J. Nicol, M.A., D.Sc. Edin., and Thomas Turner, Assoc.R.S.M., F.C.S.

Demonstrator.—T. Rhymer Marshall, D.Sc. Edin.

The Session will be opened on Wednesday, September 30th, 1891.

Elementary Course.

Forty Lectures adapted to the requirements of beginners will be given in the Winter and Spring Terms. A Second Course of Twenty Lectures, having reference only to the subjects included in the syllabus of the Matriculation Examination of the University of London, will be given in the Summer Term. Lecture days—Wednesdays and Fridays at 11.30, Thursdays at 3.30.

Persons entirely unacquainted with Chemistry are recommended to attend the first of these Courses before entering for the General Course, which commences in October. Candidates for the Matriculation Examination of the University of London are advised to attend both these Courses.

General Course.

The General Course of Lectures on Chemistry will be found useful by Students who are afterwards to become Engineers, Architects, Builders, Brewers, or Manufacturers (such as Metallurgists, Alkali, Soap, Manure, Glass, or Cement Makers, Bleachers and Dyers, &c.)

Students preparing for the Intermediate Examination in Science and Preliminary Scientific (M.B.) Examination of the University of London should attend the Lectures on Inorganic Chemistry (Winter and Spring Terms).

Candidates for B.Sc. and Intermediate Examinations in Medicine will in general require only that part of the course (Summer Term) which relates to Organic Chemistry.

The full course, extending over three terms, will also satisfy the requirements of Students preparing for the Associateship of the Institute of Chemistry, so far as attendance at lectures on General and Theoretical Chemistry is concerned.

1. From October to March (Winter and Spring Terms). About eighty lectures on Inorganic Chemistry and Chemical Philosophy will be given on Mondays, Tuesdays, Wednesdays, and Thursdays from October to December, and on Mondays, Tuesdays, and Wednesdays from January to March, at 9.30 a.m. Fee, £5 5s. for the course.

2. April to June (Summer Term). About thirty lectures will be given on Elementary Organic Chemistry, or the chemistry of the most important series of carbon compounds. This course will include all the subjects required for the Intermediate Examination in Medicine of the University of London. Lecture Days—Monday, Tuesday, Wednesday, and Thursday at 9.30 a.m. Fee, £1 11s. 6d.

Advanced Course.

An Advanced Course for the study of Theoretical Chemistry and those parts of the subject which are required for the degree of B.Sc. in the University of London will meet once or twice a week. Fee for the session, £3 3s.

Laboratory Practice.

The College Laboratory is open daily from 9.30 to 5, except on Saturdays, when it is closed at 1 p.m.

Candidates for Intermediate Examination in Science, Preliminary Scientific (M.B.), B.Sc., and Intermediate Examination in Medicine of the University of London, may obtain in the Laboratory of the College the instruction necessary. The three months Course of Practical Chemistry for the B.Sc., Edinburgh, in the department of Public Health, may be taken in the Mason College Laboratory. Fees :—

	All day.	Three hours per day.
One Term	7 guineas	4½ guineas.
Two Terms	13 „	8½ „
Threee Terms	18 „	12 „

A Course of short demonstrations and exercises is given by the Professor or one of his Assistants once a week. All first-year Students are required to attend, unless exempted for special reasons by the Professor. No Fee.

Metallurgy.

Three Courses of Ten Lectures will be given on the Principles and Practice of Metallurgy. Fee, 10s. 6d. for each course. A more advanced course upon selected subjects is also given by Mr. Turner, the Lecturer in Metallurgy.

There is a separate laboratory for metallurgical students in which provision is made for instruction in assaying, &c.

Evening Classes.

Several Courses of Evening Lectures are arranged during the Winter and Spring Terms of each session. The subjects are treated in a less technical manner and the fees are nominal.

Excursions.

During previous Sessions permission has been obtained to visit some of the great factories in or near Birmingham, in which chemical and metallurgical industries are carried on. Students have thus had most valuable opportunities of gaining a practical acquaintance with some branches of Applied Science. The privilege thus courteously granted by several manufacturers will, it is hoped, be enjoyed in every future Session. The excursions will be conducted by the Professor.

BRADFORD TECHNICAL COLLEGE.
CHEMISTRY AND DYEING DEPARTMENT.

Professor.—Christopher Rawson, F.I.C., F.C.S.
Demonstrator.—(Vacant).
Lecturer on Botany and Materia Medica.—William West, F.L.S.

The school year is divided into three terms. The Session commences on September 14th and terminates on July 9th. The course of instruction extends over two years, and embraces Lecture Courses on Inorganic and Organic Chemistry, the technology of the textile fibres, mordants, natural and artificial colouring matters, technical analysis, and laboratory practice in analytical chemistry, chemical preparations, and dyeing. Inclusive fee, £4 4s. per term.

During the first and second terms Evening Classes are held for the benefit of persons engaged during the day and for pharmaceutical students.

ROYAL AGRICULTURAL COLLEGE, CIRENCESTER.
CHEMICAL DEPARTMENT.

Professor.—Prof. E. Kinch, F.C.S., F.I.C.
Assistants.—James Hendrick, B.Sc. Lond., A.I.C., and W. James.

Systematic courses of Lectures are given on the various branches of Chemistry in its relation to Agriculture, illustrated by experiments, and by the collections in the College Museum. They comprise the laws of Chemical Combination and the general Chemistry of mineral bodies, and of the more frequently occurring bodies of organic origin, with the relationships of their leading groups; and, finally, the applications to practical operations of the Chemistry of the atmosphere, of soils and manures, of vegetation and stock feeding, and of the processes and products of the dairy.

In the Laboratory practical instruction is given in the construction and use of apparatus and in Chemical manipulation and analysis, both qualitative and quantitative. After studying the simple operations and the

properties of the commonly occurring substances, the Students are taught to analyse a series of compounds, and apply the knowledge thus obtained to the analysis of manures, soils, waters, feeding stuffs, dairy products, and other substances met with in the ordinary course of Agricultural practice. Chemico-agricultural researches are undertaken by the senior Students under the direction of the Professor and his Assistants.

VICTORIA UNIVERSITY.
THE YORKSHIRE COLLEGE, LEEDS.

Professor of Chemistry.—Arthur Smithells, B.Sc. Lond., F.I.C.
Assistant Lecturer in Organic Chemistry. — Julius B. Cohen, Ph.D., F.I.C.
Assistant Lecturer in Agricultural Chemistry.—Herbert Ingle, F.I.C.
Demonstrator.—J. H. Davies, B.Sc.

The Session begins October 6, 1891.

Lecture Courses.

1. General Course of Chemistry.—Monday, Wednesday, and Friday, at 11.30 a.m., from October to the end of the second term, and during part of the third term. Fee for the Course, £4 4s.

2. Inorganic Chemistry.—First year Honours Course, Non-metals. Monday, Wednesday, and Friday, at 9.30 a.m. Fee, £3 13s. 6d.

3. Inorganic Chemistry. — Second year Honours Course, Metals. Tuesday, Thursday, and Saturday at 9.30 a.m. Fee, £3 13s. 6d.

4. Organic Chemistry. — Tuesday, Thursday, and Saturday at 11.30 p.m. Fee £3 13s. 6d.

5. Organic Chemistry Honours Course.—Monday and Wednesday at 9.30 a.m. Fee, £2 12s. 6d.

6. Theoretical Chemistry.—Advanced Course. Tuesdays and Thursdays at 9.30 a.m. Fee, £2 12s. 6d.

7. Chemistry as Applied to Coal Mining.— Tuesday during the First Term, at 4 p.m.

8. Agricultural Chemistry.—Monday, Tuesday, and Friday, at 3 p.m., during first and second terms.

Laboratory Courses.

The College Laboratory will be open daily from 9 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it will close at 1 p.m.

Fees for the Session—Students working six days per week, £18 18s.; five, £16 16s.; four, £14 14s.; three, £12 12s.

Class in Practical Chemistry, Saturday mornings, from 9.30 to 12.30. Fee £1 11s. 6d.

Practical Chemistry for Medical Students.—On Tuesday and Thursday, from 10 to 12 a.m., from May to July.

Practical Course in Sanitary Chemistry at times to be arranged.

Evening Class.

A Course of twenty Lectures by Mr. Ingle, on the Elements of Inorganic Chemistry (the Non-Metals) will begin during the first and second Terms, on Wednesdays, at 7.30 p.m., beginning October 14. Fee, 10s. 6d.

Dyeing Department.

Professor.—J. J. Hummel, F.I.C.
Lecturer.—L. Liechti.
Assistant Lecturers.—W. M. Gardner and A. B. Knaggs.

This Course extends over a period of three years, and is intended for those who wish to obtain a full scientific and practical education in the art of dyeing. It is suitable for those who purpose in the future to take any part in the direction of the operations of dyeing or printing of textile fabrics, *e.g.*, the sons of manufacturers, calico printers, managers, master dyers, &c.

Leather Industries Department.

Lecturer.—H. R. Procter, F.I.C.

The full Course, which extends over a period of three years, is suitable to all who intend to become Technical Chemists in the Leather Industry, or managers of im-

portant works, and is recommended to sons of tanners. The Course includes instruction in chemistry, engineering, microscopy, leather manufacture, and practical work in the Leather Industries Laboratory.

Agricultural Department.

Professor.—James Muir.

The full Course occupies two years, and includes instruction in chemistry, physics, botany, engineering and surveying, and the principles of agriculture, as well as practical work in the various laboratories and out-door agriculture.

Research Students are admitted to the College Laboratories on reduced terms.

Several valuable Scholarships are at the disposal of the College, viz., the Cavendish, Salt, Akroyd, Brown, Emsley, Craven, and Clothworkers' Scholarships, and the Leighton Trustees' Exhibition, and one of the new 1851 Exhibition Scholarships. The West Riding County Council Scholarships are tenable at the Yorkshire College.

UNIVERSITY COLLEGE, LIVERPOOL.

Professor.—J. Campbell Brown, D.Sc.

Demonstrators and Assistant Lecturers.—C. A. Kohn, B.Sc., Ph.D., T. L. Bailey, Ph.D., and W. H. Ince, Ph.D.

Assistant.—H. H. Froysell.

The Session commences October 1st.

The Classes meet the requirements of candidates for the Ordinary B.Sc. Degree, for Chemistry Honours, or for the D.Sc. Degree in Victoria University; for Degrees in Medicine of Victoria, London, and Edinburgh; for a special Technological Certificate of University College; and for those studying Chemistry as a preparation for professional, technical, or commercial life. The Classes qualify for the Fellowship of the Institute of Chemistry of Great Britain and Ireland, and other Examination Boards.

Lecture Courses.

General Elementary Course on the principal non-metallic elements and the most important metals, the principles of Chemical Philosophy, and an introductory sketch of Organic Chemistry. Three Terms. Fee, £4.

Course A.—Non-metals. Fee, £3 10s.

Course B.—Metals. Fee, £3.

Course C.—Organic Chemistry. Three Terms. Fee, £3.

Course D.—Physical Chemistry. One Term. Fee, £1.

Course E.—History of Chemistry and of the Development of Modern Chemical Philosophy. Three Terms. Fee, £2.

Course F.—Technological Chemistry: Lectures on Technology are given in connection with Laboratory work at hours to be arranged. The subjects are varied in different years. (1) Alkali and Allied Manufactures. (2) Copper, Iron, and Steel. (3) Lead, Silver and Gold, Aluminium, and other Metals. (4) Distillation of Coal and Tar Industries. (5) Fuel. (6) Chemistry Applied to Sanitation. (7) Technical Gas Analysis. (8) Spectroscopy.

Practical Classes.

(1) Junior. (2) Intermediate: Qualitative Analysis of Inorganic Substances and of some of the more common Organic Substances. (3) Special: For the Conjoint Board of Colleges of Physicians and Surgeons. (4). Senior: Practical Organic (Advanced Medical Class). (5) Practical Exercises on Technology, Pharmaceutical Chemistry, Sanitary subjects, Adulterations of Drugs and of Food, Examination of Water and Air, of Animal Secretions, Urinary Deposits, Calculi, and Poisons. (6) Quantitative Class: Course arranged to suit the requirements of the London University B.Sc. Examinations, Pass and Honours, and for Inter-mediate M.B. Honours.

Chemical Laboratory.

The Chemical Laboratories provide accommodation for every kind of chemical work.

Students desirous of gaining a thorough theoretical and practical acquaintance with Technical Chemistry, or who intend to adopt Chemical work as a profession, must devote three or four years to special study.

TABLE OF FEES.

Per Week.	One Month.	One Term, Three Months.	Two Terms, Six Months.	Three Terms, One Session.
One day ..	—	£4	—	£8
Two days ..	—	6	—	10
Three days..	£4	8	—	12
Four days ..	4	9	12	15
Five days ..	—	10	14	18

Technological Curriculum.

Preliminary Year.—Chemistry, either the Elementary Course or Course A, according to the previous knowledge of the Student. Practical Classes 1 and 2. Mathematics, or Mechanics, or Physics. Engineering Drawing and Design (in this or one of the following years). French or German.

First Year.—Chemistry—Courses A and B; Chemical Laboratory three days per week; Practical Organic Class during the Summer Term; Technological Chemistry, Course F. Physics, with laboratory work, one day per week. Mathematics (intermediate). German; Intermediate B.Sc. Examination may be passed. Engineering, First Year Course, Autumn and Lent Terms.

Second Year.—Chemistry, Lecture Course on Organic Chemistry, C, Lecture Course E or D, Technological Chemistry, Course F. Chemical Laboratory, four days per week. Engineering, Mathematics, or Physics (Advanced). The Final Examination for the Victoria B.Sc. may be taken.

Third Year.—Courses D and F; part of Course C. Any other Courses omitted in a previous year. Laboratory, five days per week. Students may finally choose a special subject either of research or of applied Chemistry. The Examination for the Associateship of the Institute of Chemistry of Great Britain and Ireland may be taken. Three years study after passing the Preliminary Examination of Victoria University are required for the B.Sc. Degree in the Honours School of Chemistry.

Evening Classes.

Lectures will be given on the Products of the Destructive Distillation of Coal, Coal Gas, Coal Tar, and Ammonia; on Fuel; and on Practical Chemistry with Exercises.

The Sheridan Muspratt Chemical Scholarship of £50 per annum, tenable for two years, and a Sheridan Muspratt Exhibition of £25 per one year, will be awarded in December, 1891, on an Examination in subjects which are included in the first two years of the above curriculum. Other Scholarships, Entrance Scholarships, and Free Studentships are also available to Students.

The Prospectus containing full particulars may be obtained from the Registrar, University College, Liverpool.

LIVERPOOL COLLEGE OF CHEMISTRY.

Principal.—George Tate, Ph.D., F.I.C., F.C.S.

The Laboratories are open daily from 10 to 5, excepting Saturdays, when they close at 1 p.m. The course of instruction is adapted to the requirements of students of Chemistry as a science, and in its applications to chemical and metallurgical industries. The fee for a three years' course of study is eighty guineas, or per session of three months eight guineas.

Prospectuses, containing full particulars of the day and evening classes, may be had on application at the College

DURHAM COLLEGE OF SCIENCE, NEWCASTLE-ON-TYNE.

Professor of Chemistry.—P. Phillips Bedson, D.Sc., F.C.S.

Lecturer in Chemistry—Saville Shaw, F.C.S.

Lecturer in Agricultural Chemistry.—W. C. Mackenzie, D.Sc. (Edin.).

The Session will commence on September 28th, 1891.

1. *General Course.* — This Course of Lectures will extend over the three terms of the Session, and is intended to serve as an introduction to the Science.

The Lectures will be of an elementary character, and whilst framed to meet the requirements of First Year Students will also be serviceable to such as intend pursuing Chemistry in its various applications in the arts and manufactures, as, for instance, Brewing, Metallurgy, the Manufacture of Soda, Soap, Glass, &c. The subjects treated will include an exposition of the Principles of Chemistry, and a description of the preparation and properties of the chief Elementary Substances, both metallic and non-metallic, and their more important native and artificial compounds. A section of this Course will be devoted to an outline of Organic Chemistry. The class will meet on Mondays, Wednesdays, and Fridays, at 11.15 a.m., and will commence on Wednesday, October 7th.

Fee, £3 10s. for the Session.

2. *Advanced Course.*—Inorganic Chemistry, Tuesdays and Fridays, 3 to 4 p.m., during Michaelmas and Epiphany Terms.

3. *Organic Chemistry.* — A Course of about ninety Lectures will be given throughout the Session, the subject of which will be Organic Chemistry, or the Chemistry of the Carbon Compounds. This class will meet on Tuesdays and Thursdays, at 11 a m., and will commence on Tuesday, October 8th.

Fee, £3 10s. for the Session.

Advanced Classes will be formed for the study of Inorganic, Organic, and Theoretical Chemistry. Fee for each course, £2 2s.

A Lecture Course in Analytical Chemistry will be given on Mondays, at 3 p.m., commencing October 12th. Fee, £1 1s.

Metallurgy and Assaying.—A Metallurgical Laboratory is provided, in which instruction is given in the ordinary processes of Dry-Assaying, and in the preparation and analysis of Alloys, &c. Fee as for Chemical Laboratory.

Agricultural Chemistry.—The instruction in this branch of Chemistry will consist of a series of Lectures and of special practical work in the Chemical Laboratory. Students will be expected to have a knowledge of Elementary Chemistry, such as may be obtained by attending the General Course.

A Lecture Course in Agricultural Chemistry will be given on Tuesdays and Thursdays at 10—11. Fee, Two Guineas.

Practical Chemistry.—The Laboratory is open from 10 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it closes at 1 p.m. *Laboratory Fees.*—Students working six days per week, £5 5s. per term; alternate days, £3 3s.; one day per week, £1 1s.

Courses of Study.—Students will be divided into two classes :—(1) Regular, or Matriculated Students; and (2) Non-Matriculated Students. Regular Students will be required to follow such a course of study in the subjects professed in the College as will enable them to pass the Examinations for the title of Associate in Physical Science. Non-Matriculated Students will attend such classes as they may select. Every candidate for admission as a matriculated student must pass an examination on entrance, in reading, writing from dictation, English or Latin Grammar, arithmetic (including decimals), and geography. Registered students in medicine are exempted from this examination, or students who produce a certificate of having passed either of the two following examinations :—

1. Durham Examination for certificate of proficiency in General Education, held in March and September.

2. Durham Examination for Students in Arts in their first year, or any examination of a similar nature that may be accepted by the Council.

Associateship in Physical Science.—Every candidate for the Associateship in Physical Science will be required to satisfy the examiners in three, at least, of the five subjects,—Mathematics, Physics, Chemistry, Geology, and Biology,—in an examination, to be held at the beginning of his second year.

Exhibitions.—Three Exhibitions of the value of £25, £15, and £10 respectively will be awarded in October next to Candidates desirous of attending the first year course of study in the College.

The examination will be held at the College, and wil commence on Monday, September 29th.

Evening Lectures. —Courses of Evening Lectures will be given, with a Practical Class for Laboratory instruction.

Two Exhibitions of £15 each will be awarded at the next examination of " Persons not members of the University," which will be held at Durham in March next.

Several other valuable Scholarships are available for students.

OWENS COLLEGE,
VICTORIA UNIVERSITY, MANCHESTER.

Professor and Director of the Chemical Laboratory.—Harold B. Dixon, M.A., F.R.S.

Professor of Organic Chemistry.—C. Schorlemmer, LL.D., F.R.S.

Demonstrators and Assistant Lecturers.— Julius B. Cohen, Ph.D., and George H. Bailey, D.Sc., Ph.D.

Assistant Demonstrators.—A. Harden, M.Sc., Ph.D., and G. Fowler, M.Sc.

Lecturer in Dyeing and Printing.—Ernest Bentz.

The Session begins on October 6, 1891, and ends on June 24, 1892.

The instruction is given by means of Experimental Lectures and Tutorial Classes. The Chemical Classes form part of the Courses for Chemistry in the University.

General Chemistry.

General Chemistry Course.—Tuesdays, Thursdays, and Saturdays, at 9.30, during the two Winter Terms.

Introduction to Organic Chemistry.—Wednesdays and Fridays, at 10.30, during Lent Term.

These courses are intended for Medical Students and others beginning the study of chemistry.

First Year Honour Course.—Mondays, Wednesdays, and Fridays, 3.30 p.m., during the two Winter Terms. The Non-Metals.

Second Year Honour Course.—Mondays, Wednesdays, Fridays, 9.30, during the two Winter Terms. The Metals.

Third Year Honour Course.—At times to be arranged. Physical Chemistry.

Organic Chemistry (Honours).—Tuesdays, Thursdays, Saturdays, 9.30, during the Session.

History of Chemistry and Chemical Philosophy.—Thursdays, 10.30, during the Session.

An ordinary degree of B.Sc. in Chemistry, Victoria University, may be taken at the College in either two or three years, according as the student passes the Preliminary Examination on joining the College or whether he takes a year to prepare for that examination. The Degree of B.Sc. with Honours in Chemistry can be taken in three years, and the College Certificate in Technological Chemistry may be taken in the same time.

A number of important Exhibitions, &c., are available to students.

Technological Chemistry.

First Course.—Sulphuric Acid and Alkali Manufactures. General Principles of Chemical Engineering.

Second Course.—The Chemistry of Fuel. The Manufacture of Illuminating Gas and Gaseous Fuel.

Third Course.—The Chemistry of Coal Tar.

Fourth Course.—Natural and Artificial Dye-stuffs.

Fifth Course.—Calico-printing.

Certificates in Applied Chemistry.

The course extends over a period of three years, and comprises systematic instruction by means of lectures and practical work in the laboratories.

Before admission to the first year's course students are required to give such evidence of elementary knowledge of Mathematics and Chemistry as shall be considered satisfactory by the Senate.

The first year's course is the same for all students working for the certificate.

In the second and third years a choice may be made between Inorganic and Organic Chemistry. By this division of the subject a student wishing to apply himself specially to the inorganic side of the science, may attend during his second year the Honours course in Metals, and courses on Geology or Mineralogy, and during his third year, courses on Metallurgy and on Geology or Mineralogy; while a student wishing to apply himself specially to the organic side of the science, may attend during his second and third years the Honours Course on Organic Chemistry, and courses on the Coal Tar Colours and on Dyeing and Printing.

Part of the Laboratory practice in the second and third years will consist in the examination and analysis of raw materials, products from chemical works, &c., in connection with the special courses of lectures on Applied Chemistry. In the Chemstry and Physic laboratories the practical work in the second year will be arranged in accordance with the branch of Chemistry selected by the candidate.

In the third year the student, if sufficiently advanced, will be set to work on some analytical process or problem in Applied Chemistry, under the direction of the teaching staff.

UNIVERSITY COLLEGE, NOTTINGHAM.
DEPARTMENT OF CHEMISTRY.

Professor of Chemistry—Frank Clowes, D.Sc. Lond., F.I.C.

Demonstrators.—J. B. Coleman, A.R.C.Sc. Dublin, F.I.C., and R. L. Whiteley, F.I.C.

Lecturers.—J. B. Coleman, F.I.C.; R. L. Whiteley, F.I.C.; C. Haydon White, M.R.C.S.; J. W. Carr, M.A.; and F. R. Sargeant.

The Classes of the College are open to students of both sexes above sixteen years of age.

The dates of commencement and end of Terms in the Session 1891-92 will be as follows:—First Term, October 5th to December 19th; Second Term, January 18th to April 9th; Third Term, April 25th to July 2nd.

Lecture Courses.—The Chemistry Day Lectures extend over three years. In the first year a student enters for the course on Non-Metals for the first two terms and for Elementary Organic Chemistry in the third term. In his second year he takes the course on Metals for the first two terms, and Advanced Organic Chemistry in the third term. In his third year he attends a course on Applied Chemistry during the first two terms. Fee for Day Lectures and Classes, 50s. for the session of three terms: Non-Metals or Metals 42s.: Organic Chemistry (one term) 21s.: Applied Chemistry, 30s.

Demonstrations and Lectures on Analytical Chemistry will be given in the day and evening, and should be attended by all students.

A Chemical Calculation Class is also held. Fee per Term, 2s. 6d.

Students may qualify themselves by attendance at these lectures and classes for the Examinations of the Universities of London, Cambridge, or Oxford, and for the Medical Examinations of the Royal College of Surgeons and of the Universities of Cambridge and Edinburgh: they may also obtain instruction in Chemistry for technical or other purposes, and can enter for a full Chemical Engineering Curriculum. Special attention is given to the requirements of candidates for the Associateship of the Institute of Chemistry.

Practical Chemistry.—The chemical laboratory is open every day except Saturday from 10 to 5, on Saturday from 10 to 12, and on Tuesday and Thursday evenings from 7 to 9. Each Student works independently of other Students at a course recommended by the Professor. Instruction is given in general Chemical Manipulation and in Qualitative and Quantitative Analysis; and students are enabled to work out the applications of Chemistry to Pharmacy, Dyeing, Agriculture, Brewing, Iron and Steel, Tanning, and other Manufacturing Processes. Fees.—For one term, £6; for the session, £15;

for day students for six hours weekly 40s., and 5s. extra for each additional hour per week. For evening students, 10s. for one evening per week, and 20s. for two evenings per week, per term.

Courses of Technical Chemistry Lectures are also given on Dyeing and Bleaching, Brewing, Bread-making, Gas Manufacture, and on other processes of applied Chemistry.

A Pharmaceutical Curriculum extending over three Winter Sessions, includes Pharmaceutical Chemistry (lectures and laboratory work), Pharmaceutical Botany (lectures and class work on specimens), Materia Medica (lectures and use of specimens), and Practical Dispensing, taught by demonstrations and practical work in the laboratory.

Government Lectures and Classes.—Evening Lectures and Laboratory instruction will be given by the Demonrators of Chemistry to Students who intend to present themselves for Examination by the Government Science and Art Department in May next. Inorganic, organic, and practical chemistry, agricultural chemistry, and metallurgy will be taught in the elementary, advanced, and honours stages, each of which commences at the beginning of the College Session in October. Fee for each Lecture Course, 2s. 6d.; for each Laboratory Course, 10s.

Full information concerning all College Classes is given in the College Prospectus, price one penny.

FIRTH COLLEGE, SHEFFIELD.

Professor of Chemistry.—W. Carleton Williams, B.Sc. F.C.S.

Demonstrator and Assistant Lecturer.—L. T. O'Shea, B.Sc., F.C.S.

Assistant Demonstrator not yet appointed.

The Session will commence on Friday, October 2.

First Year's Course.—Chemistry of the Non-Metallic Elements. Monday, Wednesday, Thursday, from 10 to 11 a.m. Fee, £3 3s.

Second Year's Course.—Chemistry of Metals. Tuesday, Wednesday, and Thursday, from 10 to 11 a.m. £3 3s.; or for the First and Second Courses, £5 5s.

Third Year's Course.—Organic Chemistry, on Wednesday, from 9 to 10, and Saturday, from 10 to 11. Fee, £2 2s.

A Course of Lectures is arranged for Medical Students, with a special class in Qualitative Analysis.

Laboratory.—Working hours to be arranged between Professor and Students.

Sessional Fees for Day Students:—Six hours per week, £5 5s.; Nine, £7; Twelve, £8 8s.; Eighteen, £11 5s.: Twenty-four, £14; Thirty-two, £17.

Day Students may not enter for less than six hours a week. Students joining the Laboratory at Christmas will be charged two-thirds and at Easter one-third of the Fees for the whole Session.

Fees for short periods (working thirty-two hours per week):—For one month, £3 3s.; two months, £5 5s.

An arrangement has been entered into with the Science and Art Department, South Kensington, which will enable Science Teachers to work in the Chemical Laboratory for three, six, or twelve hours a week on payment of one-quarter of the usual fee, the Department being willing to pay the remainder under certain conditions, of which full information may be obtained on application to the Registrar.

Evening Classes.—Lectures, Wednesday, 8 to 9. Laboratory instruction, Wednesday, 6 to 9, and another series to be arranged if desired. Sessional Fee, one evening per week, £1 10s.; two, 50s.; or Lecture Class and Laboratory, on Wednesday evening, £1 10s.

UNIVERSITY COLLEGE, DUNDEE.
(UNIVERSITY OF ST. ANDREWS).

Professor. — Percy F. Frankland, Ph.D., B.Sc. F.R.S., &c.

Assistant Lecturers and Demonstrators.—F. J. Hambly, F.C.S., and J. R. Appleyard, F.C.S.

The ninth session of the College will be opened on October 13th, 1891.

The Lectures and Laboratory practice in this University are recognised by the Royal College of Physicians and Royal College of Surgeons, London, and by the Royal College of Surgeons, Edinburgh, and for degrees in Science and Medicine by the Universities of Edinburgh, Glasgow, and Aberdeen.

The courses are suitable for the Degrees of the London University and for the Civil Service appointments, and will also satisfy the requirements of students in Pharmacy, and of students who intend to become candidates for the Associateship of the Institute of Chemistry, so far as attendance at lectures on General and Theoretical Chemistry is concerned.

Lecture Courses.

The object of these courses will be (1) to give systematic instruction in the general principles of the science, and information regarding the elements and their more important compounds; (2) to show how this knowledge may be usefully applied in the Arts and Manufactures.

A course of instruction in Practical Chemistry in the Laboratory is recommended to all who wish to obtain a sound knowledge of the science, and the methods of applying it to useful purposes—the duration of such course depending upon the special wants of the student.—The Professor will be glad to give any information to intending students.

First year's lecture course : General Chemistry (Non-Metals, Metals, and Elements of Organic Chemistry) (100 lectures), Monday, Tuesday, Wednesday, Thursday, and Friday, from 10 to 11 a.m.; fee, £3 3s.

Second year's lecture course : 1. Advanced Inorganic Chemistry, including modern Chemical Theory (50 lectures). 2. Organic Chemistry (50 lectures). Fee for the whole course, £3 3s.

A Lecture Course on Analytical Chemistry will be given on Saturdays, from 9 to 10. Fee, £1 1s.

Courses of lectures will be given on Dyeing, Bleaching, and the Chemistry of the Textile Fibres, with practical instruction in the Laboratory and Dyehouse. In connection with this Department there is an extensive Technical Museum, containing a large collection of specimens illustrating many branches of Applied Chemistry, and particularly the local industries.

Practical Chemistry (Laboratory).

The aim of the Laboratory Courses is to make the student practically acquainted with the science, so that he may conduct chemical analysis and original research, and generally to fit him for applying the science to the Arts, Manufactures, Agriculture, and Public Health. The courses are also arranged for students preparing for their medical and pharmaceutical examinations. A three months' course of practical instruction in Sanitary Chemistry for the B.Sc. Edinburgh, in the department of Public Health, may be taken in the College Laboratory.

The Laboratory will be open for students daily from 9 a.m. to 4 p.m., except on Saturdays, when it will be closed at 3 p.m. Each student on entering will be allowed to arrange his working hours to suit his own convenience, but will be required to keep the hours when once fixed.

Sessional Fees for Day Students :—The fees for both sessions are—for six hours per week, £3 3s. ; each additional hour per week, 10s. 6d. Day students may not enter for less than six hours a week. Students joining the Laboratory during the second term will be charged two-thirds, and during the third term one-third of the above fees. Students may also enter for short periods, working every day in the week at the following fees :—For one month, £2 12s. 6d. ; for two months, £5 5s. ; for three months, £7 7s.

Evening Classes.—Courses of Lectures and Practical Laboratory instruction are given in Chemistry, Dyeing, and Bleaching.

Forster Research Scholarship.

This scholarship, of the value of £30, is awarded annually to the best student on the condition that he devotes himself during the ensuing year to original research in the College Laboratory.

UNIVERSITY OF EDINBURGH.
DEPARTMENT OF CHEMISTRY.

Professor.—Alex. Crum Brown, M.D., D.Sc., F.R.S., Pres. C.S.

Assistants.—J. Gibson, Ph.D.; L. Dobbin, Ph.D.; H. Marshall, D.Sc.; J. Walker, Ph.D., D.Sc.; J. S. Murray, D.Sc.

The working terms are—Winter Session, from middle of October to middle of March ; Summer Session, from beginning of May to end of July.

Lecture Courses.—During the Winter Session a General Course of Chemistry for medical and science students is given by the Professor. The class meets daily; fee £4 4s. A class for advanced students is held in summer : it meets thrice weekly ; fee £2 2s.

In addition to the above, Lecture Courses are given by the Assistants on special subjects, such as Chemical Theory, Physical Chemistry, or some particular branch of Organic and Inorganic Chemistry. These lectures are free to Laboratory Students.

Tutorial classes are held in connection with the General Course.

Laboratories.—Practical classes for Medical Students meet daily during the latter part of the Winter Session and in the Summer Session. (Fee, £3 3s.) The laboratories for analytical and advanced practical work are open daily from 10 till 4. (Fees: Winter Session, £10 10s.; Summer Session, £6 6s.) Full Courses of instruction are given in Analytical, Practical Organic and Inorganic Chemistry. Facilities are afforded to advanced students who desire to undertake chemical investigations.

Various prizes and scholarships are attached to the laboratory and general class.

Graduation.—Two Degrees in Science are conferred, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.).

Candidates for Degrees in Science must pass a preliminary examination in English, Latin, Arithmetic, Mechanics, Mathematics, and in two of the following subjects :—Greek, French, German, Higher Mathematics, Natural Philosophy, Logic, Moral Philosophy.

The First B.Sc. Examination embraces Mathematics, Natural Philosophy, Chemistry, Zoology, and Botany. The Second B.Sc. Examination (Section b, the Physical Experimental Sciences) includes Experimental Physics, Inorganic Chemistry, Organic Chemistry, Relation between Chemical and Physical Properties, Complex Qualitative Analysis (practical), and Simple Quantitative Determinations (practical).

A candidate for the D.Sc. Degree must submit a thesis on original work done by him, a historical or critical research connected with the special subjects of his Examination. The Thesis must be approved before the candidate is allowed to proceed to Examination. The candidate in Section III. (Chemistry) will be required to pass a searching examination in one of the following branches :—(1) The Chemistry and Chemical Technology of Inorganic Bodies, including Metallurgy ; (2) Organic Chemistry ; and to show a thorough practical acquaintance with chemical analysis in all its branches, and with the preparation of pure substances.

HERIOT-WATT COLLEGE, EDINBURGH.

Professor.—W. H. Perkin, Jun., Ph.D., F.R.S.
Assistant Professor.—Arthur W. Bishop, Ph.D.
Demonstrator.—Bertram Prentice.

The Session begins October 1st, 1891.

The curriculum of this College comprises both Day and Evening Classes, each department providing the higher general and technical education.

The Lecture Course in Chemistry is mainly devoted to Inorganic Chemistry. In the Laboratory course each student is required to prepare and study the properties of the principal elementary and compound gases; to perform the more important experiments shown by the Professor in the Lecture Room; to make himself thoroughly acquainted with the preparation and purification of salts, and with the tests employed in identifying these. After a careful study of the reactions of the principal metals and acids, he passes on to a complete course of the systematic qualitative analysis of simple salts and mixtures, and may then, if attending a second year, take up an extensive course of qualitative analysis (gravimetric and volumetric), ultimately making a speciality of any branch of the subject which may be most necessary for his future work. Great attention has been paid to the thorough equipment of the Advanced Laboratories, and special facilities are given to students who may wish to engage in any class of Research (Inorganic or Organic) whether of a purely Chemical or of a Technical nature.

GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE.

The main objects of this College are to afford a suitable education to those who wish to qualify themselves for following any industrial profession or trade, and to train teachers for technical schools. It was founded by an Order in Council, dated 26th November, 1886, according to a scheme framed by the Commissioners appointed under the provisions of the Educational Endowments (Scotland) Act, whereby Anderson's College, the Young Chair of Technical Chemistry in connection with Anderson's College, the College of Science and Arts, Allan's Glen's Institution, and the Atkinson Institution were placed under the management of one governing body.

The Diploma of the College is awarded to Day Students who have attended prescribed courses of instruction and passed the necessary examinations. The ordinary courses extend over three years, but arrangements are made for advanced students continuing their studies in special departments.

Copies of the Calendar for 1891-92 may be had from Mr. John Young, B.Sc., the Secretary, 38, Bath Street, Glasgow, price by post, 1s. 4d.

UNIVERSITY OF ST. ANDREWS.

UNITED COLLEGE OF ST. LEONARD AND ST. SALVATOR.
Professor of Chemistry. — T. Purdie, B.Sc., Ph.D., Assoc. R.S.M.

The Session begins on October 27th. A Competitive Examination, open to intending Students of Arts or Science, for a number of Entrance Bursaries, ranging in value from £40 to £10 each per annum, will be held during the last week of October. Two Degrees in Science are conferred by the University of St. Andrews, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.), the regulations regarding which will be found in the " University Calendar."

Lecture Course.

A Lecture is delivered by the Professor of Chemistry, at 11 o'clock, on five days in the week throughout the Winter Session. The Course commences with the study of a few typical substances, serving as an introduction to the discussion of the Laws of Chemical Combination and the Atomic Theory; the Non - metallic and Metallic Elements, with their chief compounds, are then considered; and the latter part of the Course is devoted to Elementary Organic Chemistry. Three Lectures weekly are of an elementary character, and are intended to be useful to Students of Arts who desire to study Chemistry as a branch of general education, or with the view of teaching it in schools; the remaining two Lectures weekly constitute a Supplementary Course, framed so as to meet the additional requirements of

Candidates for the Degree of Bachelor of Science and of Medical Students.

Certificates are awarded on the results of separate examinations on the subjects of the general and supplementary Lectures, and the " Forrester Prize " of about £13 is awarded to the best Student of the year.

Fee for the Session, £3 3s.

Laboratory Course.

A class in Practical Chemistry meets for two hours weekly, to which Students attending the Lectures are admitted without additional fee. The Course consists of a series of qualitative and quantitative experiments, designed to give the Student a practical acquaintance with the principles of Chemistry regarded as a subject of general education.

The Laboratory is also open during the Session from 10 a.m. to 4 p.m., for instruction in Chemical Analysis. The fee is £10 10s. for the Session. Shorter Courses of Practical Chemistry are arranged to meet the requirements of Students who cannot give so much time to the subject, the fees for which vary according to the number of hours taken weekly.

Several free places in the Laboratory will be given to Students desirous of engaging in original work. Applicants must satisfy the Professor that their studies are sufficiently advanced to admit of them prosecuting experimental research.

The Laboratory is open for purposes of research during the summer months.

QUEEN'S COLLEGE, BELFAST.

Professor.—E. A. Letts, Ph.D., F.R.S.E., F.C.S.

I.—*Chemistry.*—The lectures are delivered at 3 p.m., on the first five days of each week until the beginning of April, and on two days of each week after May 1st. The course is divided into three parts :—(1) Chemical Philosophy ; (2) Inorganic Chemistry ; (3) Organic Chemistry.

II.—*Advanced and Organic Chemistry.*—Lectures on these subjects are given from the beginning of the Session, on Tuesdays and Thursdays, at 10 a.m., until the beginning of April, and at 3 p.m. after May 1st.

III.—*Practical Chemistry.*—In this course the Students are instructed in the general methods of conducting Chemical Analyses.

IV.—*Laboratory Pupils.*—The Chemical Laboratory is open from November until the beginning of April, and from May 1st until the middle of July, on the first five days of the week, from 10 a.m. until 4 p.m. Students are admitted as working pupils on payment of a fee of £5 for the first period, or of £3 10s. for the second period (or for a single term).

QUEEN'S COLLEGE, CORK.

Professor.—(The Chair is now vacant).

The Course of Theoretical Chemistry is divided into Inorganic and Organic Chemistry.

In the first part are discussed the Laws of Combination and Affinity, Molecular Chemistry, and the History of the Non-Metallic and Metallic substances.

In the Organic portion of the Course will be considered the subjects of Organic Analysis, Organic Series, Compound Radicals and Types, Metamorphosis of Organic Bodies, History of Special Animal and Vegetable Bodies.

In treating of the Laws of Chemistry, and the History of Inorganic and Organic Bodies those points will be chiefly dwelt upon which have a practical bearing in the Arts, Medicine, Engineering, and Agriculture. Thence, during the Course, attention will be directed to the application of Chemistry to Medicine and Physiology, to Metallurgic Operations, Chemical Manufactures, Building Materials, Soils, and Manures.

Fee.—For each Sessional Course, £2. Each subsequent Course, £1.

The Chemical Laboratory is open daily except on Saturdays, from 10 to 4 o'clock, under the Superintendence

of the Professor, to Students desirous of prosecuting an extended course of qualitative and quantitative analysis, and for the purpose of original investigation in connection with the Arts, or in the higher departments of Scientific Chemistry.

The Course of Practical Chemistry consists of about thirty-nine Lectures, and will commence at the beginning of the Second Term. Fee for each Sessional Course £3.

ROYAL COLLEGE OF SCIENCE FOR IRELAND,
Stephen's Green, Dublin.
(Science and Art Department).

Professor of Chemistry.—W. N. Hartley, F.R.S.

Assistant Chemist.—T. A. Shegog, F.I.C., F.C.S., Associate of the Royal College of Science.

The Session commences on Monday, October 5th, 1891, and ends on June 22nd, 1892.

The Royal College of Science for Ireland supplies, as far as practicable, a complete course of instruction in Science applicable to the Industrial Arts, and is intended also to aid in the instruction of teachers for the local Schools of Science.

Diplomas are awarded in the Faculties of Mining, Engineering, and Manufactures. The Diploma in the Faculty of Manufactures is recognised by the Council of the Institute of Chemistry of Great Britain and Ireland as qualifying candidates for admission to the practical examinations of the Institute.

The instruction in Chemical Science includes (1) General Chemistry, (2) Chemical Manufactures, (3) Metallurgy, (4) Analytical and Experimental Chemistry, (5) Instructions in Chemical Research.

Fees payable by Associate Students in the Faculty of Manufactures :—For the entire Course—first year, £13; second year, £23; third year, £14.

Fees payable by Non-Associates :—£2 for each separate Course of Lectures. For Analytical Chemistry and Research—£2 for a special course of one month ; £5 for three months ; £9 for six months ; £12 for the entire session. For Assaying—£5 for three months ; £9 for six months ; £12 for the entire session.

The following are supplementary courses of instruction for beginners :—

Laboratory Instruction in the Theory of Chemistry. A two-months' Course. By arrangement with the Professor the hours of attendance are fixed so as to suit, as far as possible, the convenience of the students, the laboratory accommodation being limited.

A Course of Lectures on Elementary Chemistry by the Assistant Chemist, February, March, April, and May, Wednesday, 3 to 4 o'clock. Fee for the Course, 10s.

There are four Royal Scholarships of the value of £50 each yearly, with Free Education, including Laboratory Instruction, tenable for two years ; two become vacant each year ; they are awarded on the results of their examinations to Associate Students, not being Royal Exhibitioners, who have been a year in the College. There are also nine Royal Exhibitions attached to the College, of the yearly value of £50 each, with Free Education, including Laboratory Instruction, tenable for three years ; three become vacant each year, and are competed for at the May Examinations of the Department of Science and Art.

CHEMICAL LECTURES, CLASSES, AND LABORATORY INSTRUCTION.

City and Guilds of London Institute for the Advancement of Technical Education.—*Central Institution, Exhibition Road.* — Professor of Chemistry, H. E. Armstrong, Ph.D., F.R.S. The object of this Institution is to give to London a College for the higher technical education, in which advanced instruction shall be provided in those kinds of knowledge which bear upon the different branches of industry, whether Manufactures or Arts. The main purpose of the instruction given in this Institution is to point out the application of different branches of science to various manufacturing industries. In order that this instruction may be efficiently carried out, the Institution, in addition to the lecture theatres and class rooms, is fitted with laboratories, drawing offices, and workshops ; and opportunities are afforded for the prosecution of original research, with the object of the more thorough training of the students, and for the elucidation of of the theory of industrial processes. The courses of instruction are arranged to suit the requirements of—1. Persons who are training to become Technical Teachers ; 2. Persons who are preparing to enter Engineers' or Architects' offices, or Manufacturing works ; 3. Persons who desire to acquaint themselves with the scientific principles underlying the particular branch of industry in which they are engaged.

Technical College, Finsbury.—Professor of Chemistry, Raphael Meldola, F.R.S. The operations of the Technical College, Finsbury, are divided into two distinct portions : Day Classes for those who are able to devote one, two, or three years to systematic technical education ; Evening Classes for those who are engaged in industrial or commercial occupations in the daytime and who desire to receive supplementary instruction in the application of Science and of Art to the trades and manufactures in which they are concerned or employed. The College embraces the following departments :—1. Mechanical Engineering and Applied Mathematics ; 2. Electrical Engineering and Applied Physics ; 3. Industrial and Technical Chemistry ; 4. Applied Art ; 5. the Building Trades. The College is under the general direction of the Principal. Each Professor is assisted by Demonstrators. Besides these there are Lecturers and Teachers in special subjects. An examination for the admission of Students will be held at the College at 10 o'clock on Tuesday, September 29th, 1891, and the work of the Session will commence on October 7th.

Birkbeck Literary and Scientific Institution, Bream's Buildings, Chancery Lane. — *Chemistry :* Courses will be conducted, commencing October 1st, adapted for the Elementary, Advanced, and Honours Examinations of the Science and Art Department, and for the Matriculation, B.Sc., and M.B. Degrees of the London University. *Inorganic Chemistry :* Mr. G. Chaloner, F.C.S. Lectures — Elementary, Tuesdays, 8.30 p.m. ; Advanced, Thursdays, 7 p.m. ; Practical, Tuesdays, 6—8 p.m. ; Thursdays, 8—10 p.m. ; Saturdays, 7—9 p.m. *Organic Chemistry :* Mr. F. Gossling, B.Sc. Lectures— Elementary, Wednesdays, 6.30 p.m. ; Practical, Wednesdays, 7.30 p.m., Fridays, 6 p.m.

St. George's Hospital Medical School (Chemistry Department).—Lecturer, Samuel Rideal, D.Sc., F.I.C., F.C.S. Arrangements have been made for a six months' Course in Public Health Instruction for gentlemen intending to present themselves for examination by the two colleges for the Diploma of Public Health.

Charterhouse Science and Art Schools. — The Winter Session commences on Tuesday, September 22nd, 1891, under the presidency of the Rev. H. Swann, M.A. Classes are established in this institution by which instruction of a practical character is given in most of the Sciences at a very nominal fee ; whilst in Art, at an equally low rate, Students, under the direction of five competent instructors, can be advanced in their studies. Those who have leisure can, at a very moderate charge, attend the Day Classes in Art. Day Classes will also be held to prepare Candidates for Matriculation (Lond.), the Clerical, Medical (including Dental), Legal, and other Examinations. Students who aim at becoming proficient in Chemistry (Organic and Inorganic) have the opportunity of working

in a well-fitted Laboratory, capable of accommodating sixty Students. Aspirants for University Honours can at a small expense be assisted in their studies.

THE CITY SCHOOL OF CHEMISTRY AND PHARMACY, 27, Chancery Lane, London, W.C.—Principal, Mr. Maurice Williams. Assisted by Mr. T. A. Ellwood, A.I.C., F.C.S., Mr. Martin J. Cole, and Mr. E. Hayward. Theoretical and Practical Chemistry, Chemical Physics, Theoretical and Practical Pharmacy, Materia Medica, Botany, Prescription Reading, Microscopy, &c.

MIDDLESEX COLLEGE OF CHEMISTRY AND PHARMACY, 40, Charlotte Street, Portman Place.—Principal, F. H. Painter. Day and Evening Classes and Laboratory Instruction in Chemistry, Pharmacy, Materia Medica, &c.

NEW CENTRAL SCHOOL OF CHEMISTRY AND PHARMACY, 173, Marylebone Rd., London.—Mr. J. Woodland, F.C.S., Lectures are given on Chemistry, Botany, Materia Medica, Pharmacy, Latin, and Physics. Laboratory instruction.

SOUTH LONDON SCHOOL OF PHARMACY, 325, Kennington Road, S.E.—Lectures on Chemistry and Physics, by Dr. John Muter, F.R.S.E., F.I.C., Daily, at 9 a.m. (Organic) and 10 a.m. (Inorganic). Lectures on Botany daily at 12 noon, and at 2 p.m. on Materia Medica and Pharmacy, by Mr. Dodd, F.C.S. The Laboratories for Qualitative and Quantitative Analysis open daily from 9 till 5, under the direction of Mr. de Koningh, F.I.C., F.C.S. The Students' Laboratory of this Institution is specially designed to accommodate 40 Students. The Technical Laboratory is open daily from 9 till 4, and is fully fitted with all apparatus for teaching the manufacture of drugs and chemicals. Periodical Examinations of the Students are held by Visiting Examiners appointed by the Council of Education, and Medals and Certificates are awarded on the results thereof. Fees for the first three months £10 10s. (junior) and £12 12s. (senior); afterwards £2 2s. and £3 3s. per month respectively, inclusive of all departments.

THE GOLDSMITHS' INSTITUTE, New Cross, S.E.—Head of the Chemical Department, Mr. A. G. Bloxam, F.I.C. Lectures and Practical Classes, also special classes in Chemistry as applied to various arts and industries, are held in the evenings from 7.30—10.0, and are open to both sexes. Session begins October 1st. Fees per Session (October to May): Theoretical Chemistry, 5s.; Practical Chemistry, 10s. 6d.

PEOPLE'S PALACE, Mile End Road, E. (Draper's Company's Institute).—Chemistry, Mr. D. S. Macnair, Ph.D., F.C.S. The classes are open to both sexes without limit of age.

ADDEY'S SCHOOL, Church Street, Deptford.—Head Master, William Ping, F.C.S.—Day and Evening Classes.

POLYTECHNIC INSTITUTE, 309, Regent Street, London, W.—Mr. R. A. Ward and Assistants.—Evening Classes in Theoretical and Practical Chemistry, &c.. The Classes are open to both sexes. The next term commences on Monday, September 28th, 1890.

WESTMINSTER COLLEGE OF CHEMISTRY AND PHARMACY, Trinity Square, Borough, S.E. — Messrs. Wills and Wootton. Day and Evening Classes.

BRISTOL MEDICAL SCHOOL.—Mr. T. Coomber, F.C.S.

THE CLIFTON LABORATORY, Berkeley Square, Bristol. —Conducted by Ernest H. Cook, D.Sc.Lond., F.I.C., F.C.S. Students are received either as Private Pupils or Members of a Class. Instruction is given to those requiring to use science or scientific methods in Commercial and Industrial pursuits, or in preparing for Examinations.

LEEDS SCHOOL OF MEDICINE.—Prof. Smithells.

LEEDS SCHOOL OF SCIENCE AND TECHNOLOGY, Rossington Street.—Head Master and Lecturer on Chemistry: Mr. S. J. Harris, M.Sc., F.C.S.; Lecturer on Metallurgy:

Mr. A. Burrell, F.I.C., F.C.S.; Lecturers on Chemical Technology: S. J. Harris, A. Burrell, and G. W. A. Teanby. Demonstrator in Chemistry: E. Rawlins, F.C.S. The courses of instruction are adapted to the syllabus of the Science and Art Department, but facilities are offered to those who desire to work for the London University exams., or to pursue some special branch of practical chemistry or metallurgy. The Chemical Laboratory is open for three nights per week, and the Metallurgical Laboratory for two nights. There is a special course of lectures for candidates for "Honours."

INSTITUTE OF CHEMICAL TECHNOLOGY, Hackins Hey, Liverpool.—Principal, Mr. A. Norman Tate, F.I.C. The course of instruction is intended more especially for students who wish to gain a knowledge of chemistry and the allied sciences in their relation to industrial and commercial pursuits, and embraces a thorough preliminary course of theoretical chemistry and practical laboratory work, followed by instruction in chemical technology fitted to the requirements of each pupil. In addition to these chemical studies, students who desire it can enter upon a special course calculated to afford them knowledge useful in the erection and arrangement of manufactories and plant, and construction of apparatus.

"WASTE" UTILISATION LABORATORIES, 12 and 14, Paradise St., Liverpool.—Principal: H. Belcher Thornton, F.C.S.

INSTITUTE OF SCIENCE AND ART, VALPY STREET, READING.—Head Science Master: Alfred J. Shilton, F.C.S.

SHEFFIELD BOROUGH ANALYSTS' LABORATORY, 1, Surrey Street.—Mr. A. H. Allen, F.C.S. Day and Evening Classes.

STOCKPORT TECHNICAL SCHOOL. — Department of Chemistry and Dyeing.—Principal: Mr. R. J. Brown, M.Sc. Lecturer on Chemistry and Metallurgy: Mr. G. W. Davies, F.C.S. Lecturer on Dyeing and Hat Manufacture: Mr. W. M. Gardner, F.C.S. Theoretical and Practical Instruction is given in Chemistry, Metallurgy, Dyeing, Bleaching, and Hat Manufacture. A syllabus with full particulars of the courses of instruction, hours, fees, &c., is obtainable on application.

TECHNICAL INSTITUTE, SWANSEA. — Classes in Theoretical and Practical Chemistry and Practical Metallurgy will be held during the winter session, 1891-2. Principal, W. Morgan, Ph.D., F.C.S., F.I.C.

GEORGE HERIOT'S HOSPITAL SCHOOL, EDINBURGH.— Samuel Walker, M.A., B.Sc.

SCHOOL OF MEDICINE, SURGEON'S HALL, EDINBURGH.— Dr. Stevenson Macadam, F.R.S.E.

CHEMICAL LABORATORIES AND CLASS ROOMS, 4, Lindsay Place, Edinburgh.—Open throughout the year for Students, under the superintendence of J. B. Readman, D.Sc. F.R.S.E., F.C.S. Attendance at this laboratory qualifies for the Degrees of Medicine, Science, and Public Health of Edinburgh University, and for the Examinations in Medicine and Public Health of the Royal Colleges of Physicians and Surgeons, Edinburgh.

SCHOOL OF MEDICINE, MINTO HOUSE (NEW VETERINARY COLLEGE, EDINBURGH).—Mr. J. Falconer King, F.C.S., F.I.C.

ST. MUNGO'S COLLEGE AND SCHOOL OF MEDICINE, EDINBURGH.—Dr. Milne.

GLASGOW UNIVERSITY.—Prof. J. Ferguson.

CHEMICAL LABORATORIES AND CLASS ROOMS.—Messrs. R. R. Tatlock and Readman, City Analyst's Laboratory, 156, Bath Street, Glasgow; and 4, Lindsay Place, Edinburgh. The Laboratory is open daily all the year for the reception of students, under the immediate supervision of R. R. Tatlock, F.R.S.E., F.C.S., F.I.C., the City Analyst and Gas Examiner.

CITY ANALYST'S LABORATORY AND CLASS ROOMS, 138, Bath Street, Glasgow.—Messrs. Wallace and Clark. Laboratory Instruction in Analytical and Practical Chemistry.

GLASGOW VETERINARY COLLEGE.—Professor Cooke.

ANDERSON'S COLLEGE, GLASGOW.— Mr. J. R. Watson.

CHEMICAL LABORATORY, 10, Moss Street, Paisley.— Mr. Charles Manners, Jun., F.I.C. Day and Evening Classes.

FREE MUSEUM, PAISLEY.—Mr. J. M. B. Taylor. Agricultural Chemistry, Geology, Mineralogy and Botany.

STIRLING SCHOOL OF SCIENCE AND ART.— Chemical and Physical Laboratories.—Andrew Wilson, F.I.C., and Assistants.   Laboratory work daily, from 10 to 1. Lectures, 2 to 4 p.m.

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QUEEN'S COLLEGE, GALWAY.—Dr. Dixon.

ROYAL COLLEGE OF SURGEONS IN IRELAND, DUBLIN.— Professor of Chemistry and Hygiene: Sir Charles A. Cameron, M.D., F.R.C.S.I. Instruction is given in the College Laboratory in General, Practical, and Analytical Chemistry, and in the subjects (Physical, Chemical, and Microscopical) required for Examinations in Public Health and to educate for the position of Public Analyst.

DUBLIN, CARMICHAEL COLLEGE OF MEDICINE.—Professor of Chemistry: C. R. C. Tichborne, Ph.D., F.C.S.

DUBLIN, CATHOLIC UNIVERSITY.—Dr. Campbell.

CITY OF DUBLIN TECHNICAL SCHOOLS, Lower Kevin St., Dublin.—Mr. Clement J. Leaper. Evening Classes in Theoretical and Practical Chemistry.

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THE CHEMICAL NEWS.

Vol. LXIV., No. 1660.

ON THE CAUSE OF IMPERFECTIONS IN THE SURFACE OF ROLLED COPPER ALLOYS.*

By THOMAS TURNER, A.R.S.M., Mason College.

The greater part of this paper has already been published (Chemical News, vol. lxiii., p. 227). It has recently been suggested that the red stains examined by the author were possibly caused by the presence of iron, irregularly distributed through the alloy. The iron was asserted to cause electrical action during pickling, and to lead to local deposition of copper. The iron was supposed to be introduced by the workman, who generally uses an iron rod for stirring the metal in the crucible during the melting of the alloy. The author has conducted a number of experiments to test this matter, by adding different proportions of iron to zinc-copper alloys during melting, and also by rolling out a steel wire embedded in a brass ingot so as to get iron introduced in a definite and recognisable form. It would appear that iron itself has no such electrical action as has been suggested, either when alloyed or when merely embedded in the other metals. Iron rust, however, does cause a red stain on the surface of the rolled alloy, though this stain is possibly due to an absorption of the pickling liquor by the porous oxide; and the author has previously shown that the presence of a little of the pickling solution produces this effect.

Iron does not cause any red stain in yellow copper alloys if the oxide is rubbed off, or otherwise removed, at each re-heating. The fact that good surfaces are regularly produced with Delta metal, and other alloys containing iron, is regarded as proof of the correctness of the author's conclusions.

Since the previous paper was published other instances have been observed in which much trouble has been experienced from the presence of red stains on the finished metal, and in these cases, also, water rich in chlorides was used for washing the sheets after pickling.

ACTION OF NITROSYL CHLORIDE ON UNSATURATED CARBON COMPOUNDS.*

By J. J. SUDBOROUGH, B.Sc., A.I.C., F.C.S., Associate of Mason College, Birmingham.

The first investigations as to the action of nitrosyl chloride on carbon compounds were apparently made by Tilden. In 1874 this chemist studied the action of NOCl on phenol. He found that when dissolved in glacial acetic acid, and treated with NOCl gas, whilst kept in a freezing mixture, the greater part of the phenol is converted into chloranil, whilst small quantities of ammonium chloride are formed at the same time (*Journ. Chem. Soc.,* 1874, vol. xxvii., 851). A few years later the same chemist investigated the action of NOCl on the terpenes. By acting on chloroform solutions of the terpenes kept at $-10°$ he obtained compounds of the formula—

$$C_{10}H_{16}NOCl.$$
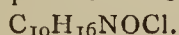
These compounds vary slightly in melting-point and other properties, according to the terpene from which they are prepared. By treating these bodies with alcoholic potash the elements of hydrochloric acid are withdrawn, and the substances known as isonitrosoterpenes are

formed (*Journ. Chem. Soc.,* 1877, vol. xxxi., 554). Two years later Tönnies investigated the action of nitrosyl chloride on amylene and anethol (*Berichte,* 1879, vol. xii., 169). Both these bodies form addition compounds, viz., $C_5H_{10}NOCl,$ and

$$C_6H_4{<}^{OCH_3}_{C_3H_5NOCl.}$$
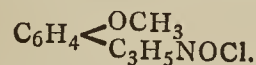
By reduction the corresponding bases are formed, viz., $C_5H_{11}NH_2,$ and

$$C_6H_4{<}^{OCH_3}_{C_3H_6NH_2.}$$
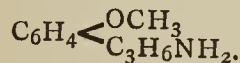
The following paper is a preliminary note on some experiments undertaken by myself during the past few months with the object of generally studying the behaviour of nitrosyl chloride towards unsaturated carbon compounds. Among the compounds which have been treated with the nitrosyl chloride are ethylene, propylene, amylene, cinnamene, crotonic, oleic, erucic and cinnamic acids. The nitrosyl chloride used throughout these experiments was prepared from dried common salt and nitrosyl sulphate. (Sudborough and Millar, *Journ. Chem. Soc.,* 1891, vol. lix., 73).

Action on Ethylene. — Ethylene, which had been thoroughly washed and dried, was passed, together with the nitrosyl chloride, through a long spiral tube, and then through two U tubes cooled to about $-15°$. By this means a quantity of a red liquid was formed, the greater part of which was condensed nitrosyl chloride. After standing for some time the nitrosyl chloride passed off, and a yellowish oil boiling at $80°$ was left behind. Another portion was distilled straight away; it began to pass over at $15°$, and the temperature gradually rose to $80°$, when a small quantity of the same oil was left behind. As this oil was not decomposed by water, the original red liquid was treated with a very dilute alkaline solution, the nitrosyl chloride was thus decomposed, and the oil fell to the bottom. This oil was washed, dried, and distilled. As thus obtained it was a colourless, fragrant liquid, boiling between $81°$ and $84°$. It was found to contain chlorine, but not nitrogen, and on analysis gave numbers which clearly showed it to be ethylene dichloride $C_2H_4Cl_2$. It also agreed with Dutch liquid in all its properties. The yield was small; after the two gases had been passing for four or five hours only about 10 c.c. of the oil were obtained. It thus appears that ethylene does not unite with nitrosyl chloride to form a stable compound, but is directly chlorinated, forming Dutch liquid $C_2H_4Cl_2$.

Action on Propylene.—Propylene obtained by the action of allyl iodide on ethyl alcohol and zinc, was treated in exactly the same way as ethylene. The red liquid thus obtained yielded only a very small quantity of oil. This oil possessed a very pungent odour, and was found to contain chlorine. Although the gases were kept passing for several hours sufficient oil was not obtained for analysis. When the propylene was allowed to bubble through liquid nitrosyl chloride, no compound of any kind was formed. In order to prove that the propylene used in these experiments was practically pure, a specimen of the dibromide, $C_3H_6Br_2$, was prepared and analysed. This compound was readily formed, and on analysis yielded good results. Hence it appears that nitrosyl chloride has practically no action on propylene.

Action on Amylene.—The following was found to be the best method of preparing the amylene nitrosochloride:—About 50 grms. of pure amylene are dissolved in an equal bulk of chloroform. The solution is kept at $-10°$, and the nitrosyl chloride gas is allowed to pass in. The liquid turns blue, and afterwards, when excess of nitrosyl chloride has been passed, a deep green. The chloroform is then evaporated off as quickly as possible, by pouring on to a plate, and blowing air through. A minutely crystalline substance, coloured blue, is thus obtained. It cannot readily be drained from a small quantity of oil formed at the same time, as it dissolves

again so readily on the slightest warmth. The best plan, therefore, is to dissolve the whole in the smallest possible quantity of alcohol, and allow to stand for several hours, when the nitroso-chloride crystallises out in large, colourless, prismatic needles. These are tolerably pure, but may be re-crystallised by spontaneous evaporation from alcohol as long needles, or from chloroform as large monoclinic tables. These crystals melt at 152°, and on further heating decompose. They are readily soluble in chloroform, ether, alcohol, lignon and water. On reduction they yield the compound $C_5H_{11}NH_2$, one of the amylamenes.

Action on Cinnamene.—Pure cinnamene, obtained from cinnamic acid, was treated in exactly the same way as the amylene. The nitrosyl chloride was passed in until the liquid was a deep red and smelt strongly of the chloride. The solution was then poured into about twice its bulk of methylated spirit, and as the chloroform gradually evaporated off minute crystals separated out. These were obtained quite pure by dissolving again in chloroform and precipitating with alcohol. As thus obtained the substance is a snow-white minutely crystalline body. On analysis it yielded results which proved it to be cinnamene nitroso-chloride, $C_6H_5 \cdot C_2H_3NOCl$. It melts at 97°, dissolves very readily in chloroform and also in ether, is only very slightly soluble in cold alcohol, but dissolves in boiling alcohol and is insoluble in water. On heating above its melting-point it decomposes, leaving a black tar which smells strongly of bitter almonds. Up to the present no base has been obtained by treating with hydriodic acid, nor yet with sodium amalgam.

Action on Crotonic Acid.—A small quantity of crotonic acid was dissolved in chloroform and treated with the nitrosyl chloride, when kept below −10° The solution became red at once, and soon smelt of nitrosyl chloride. On allowing the chloroform to evaporate away a colourless crystalline body was obtained. This melted at 68°, whereas pure crotonic acid melts at 72°. This substance was also found to contain neither chlorine nor nitrogen. Another portion of crotonic acid was dissolved in chloroform and placed in a sealed tube, when a quantity of nitrosyl chlorine was condensed on it. The tube was then sealed, and heated to about 90° on the water-bath, On allowing the chloroform to evaporate away the greater part of the crotonic acid crystallised out unaltered (m.p. 70°), although a small quantity of an oily substance was found at the same time. It therefore appears that crotonic acid is unaffected by nitrosyl chloride at any temperature between −10° and 90°.

Action on Oleic Acid.—The chloroform solution, when treated with nitrosyl chloride at −10°, turned blue, and much heat was evolved. On evaporating off the chloroform a bluish solid was left: this was washed with cold alcohol and re-crystallised from chloroform. It separated out as white waxy plates, which melted at 86°. On analysing it gave results which agreed with the formula $C_{18}H_{34}O_2NOCl$. It dissolves readily in chloroform, is only slightly soluble in cold alcohol, and insoluble in water.

Action on Erucic Acid.—This acid was treated in exactly the same way as the oleic acid, and it yielded a similar compound. This body crystallised from chloroform in waxy plates which melted at 92°, and on further heating decomposed. Analysis showed it to have the formula $C_{22}H_{42}O_2NOCl$. It agrees with the corresponding nitroso-chloride obtained from oleic acid in most of its properties. Thus both oleic and erucic acids readily unite with nitrosyl chloride to form definite compounds.

Action on Cinnamic Acid.—A chloroform solution of cinnamic acid turned red at once when treated with nitrosyl chloride at −10°. The gas was passed in till the solution smelt strongly of nitrosyl chloride, and then the chloroform was evaporated off. The only product thrown down was the unaltered cinnamic acid. A chloroform solution of the acid was then heated with a quantity of liquid nitrosyl chloride in a sealed tube to 100°. On evaporating off the chloroform, colourless crystals separated

out; these were found to contain chlorine, and analysis showed them to have the formula $C_9H_8O_2Cl_2$. An alcoholic solution of cinnamic acid was treated with amyl nitrite and hydrochloric acid, but the cinnamic acid was thrown down unaltered by the addition of the HCl. Thus cinnamic acid appears to form no addition compound, but at high temperatures is merely chlorinated to the compound $C_9H_8O_2Cl_2$.

Conclusion.—From these few experiments no definite conclusions can be arrived as to the reasons why nitrosyl chloride forms addition compounds with some unsaturated bodies, chlorinates others, and is apparently altogether without action on others. But by further and more detailed investigation it is possible that some law may be found which governs the action of the nitrosyl chloride, and this may probably be of some use in determining the constitution of the terpenes. Hence it is my intention to continue this work at some future date.

Mason College, Birmingham.

A NEW METHOD FOR THE DISPOSAL OF SEWAGE, WITH SOME REFERENCES TO SCHEMES NOW IN USE.[*]

By C. G. MOOR, B.A. Cantab.

I.

IN concluding a paper on methods of sewage treatment read at Burlington House at the recent Hygiene and Demography Congress, Dr. Thresh asked this question: "Do any of the processes mentioned, or any combination of such processes, enable us to get rid of our sewage in such a way as to give rise to no nuisance, cause no danger to health, and this at a cost sufficiently reasonable, considering the importance of attaining such results?"

In the opinion of most experts at the present day, the only answer that can be given to this enquiry is an emphatic negative.

We can see this from a brief consideration of those methods that are now in use; they may be divided into three classes:—

1. Lime processes.
2. Processes in which lime is not used.
3. Irrigation.

1. The first of these classes may be briefly disposed of; the lime is used either alone or in combination with aluminous salts, or, as in Hanson's process, with the so-called sulphurous powder. In each of these cases a good effluent is the only thing aimed at, as the sludge is worthless.

It is also worthy of notice that where lime has been used to precipitate, it must also be added to press with. Under this head also comes the Amines process, in which herring brine is added to the lime with a view of sterilising the sewage.

2. *Processes in which Lime is not used.* — The best-known of these is the A B C, in which the sewage is precipitated by a mixture of clay, alum, and charcoal, with a little blood. A clear, inodorous, and tasteless effluent is produced, and the sludge is pressed without lime, dried, and ground; it is stated to contain 3 per cent of ammonia and 5 per cent of phosphates: both of these figures seem high if the manure sold has not been enriched by ammonia or phosphate. Much has been said for and against this process; at any rate it is better that the sludge, whatever it contains, should go on the land than have to be thrown away, as sometimes happens in the lime processes.

The International Sewage Purification Company precipitate with a mixture of magnetic oxide of iron and salts of iron, alumina, and magnesia. The effluent is

further purified by passing through a filter bed of gravel and polarite. The sludge, when pressed without lime and dried, readily crumbles into a fine powder, and should be of some value as manure.

Webster's Process, or Electrical Treatment. — The sewage travels along a trough in which are placed iron plates connected to the terminals of a dynamo. Water is decomposed, and some iron also passes into solution, precipitation takes place, and the effluent is said to be good.

3. *Irrigation.*—In cases where land is cheap and of suitable character this plan may be adopted with success. In most cases the first cost is great, and so is the cost of maintenance. It is a disputed point as to whether parasites may not be communicated to the animals feeding from the crops raised off unfiltered sewage, and it is certainly not advisable, as is sometimes done, to irrigate fields with untreated sewage, so that pools of putrefying matter are formed round which cattle are feeding.

In the case of London it would be practically impossible to get land enough to deal with the enormous volume of sewage, which is very greatly increased in wet weather; and though it may be said that this is in great part rain water, yet the dirt washed off the streets and the fungus torn from the sewers by the increased volume of water will render some method of treatment as necessary as if it were ordinary sewage.

II.

And now to come to the subject of this paper; the treatment I have to lay before you has been practically tested by me at experimental sewage works at Leyton. I have no very novel suggestions as to the precipitation of sewage, the originality of my method depending on the manner in which the sludge cake, produced by any precipitation process, may be converted into marketable products.

Let us consider the ordinary composition of sludge cake; it is roughly, in 100 parts,—

Water	25
Inorganic matter containing phosphates	20
Combustible matter containing nitrogen	55

The above figures refer to sludge cake that has been dried by exposure to the air for some days.

Now suppose we could afford to distil the cake in gas retorts, we should save the ammonia; but it could not pay unless one could produce a sludge very rich in ammonia, and then it would be saleable without further treatment. There is, however, a cheaper way of distillation than that I have just mentioned. A Mr. Rees Reece, in a patent a good many years old, described a method of obtaining tar, ammonia, acetic acid, and inflammable gas from peat: this process was in successful operation for some time. He employed a kind of lime kiln with a forced draught, connected to a series of condensers. The operation was conducted in such a manner that the material in the lower part of the furnace was kept in active combustion, its heat distilled the material directly above, and this in its turn gradually descended to serve as fuel for the succeeding charge. Thus nearly the same effect was produced as if the peat had been distilled in retorts, except that, instead of carbonised matter, ash was obtained. I have employed the same method for dealing with sludge cake, and have made experiments on a sufficiently large scale to show the possibility of practical working. A furnace was set up built of boiler plate, lined with brick, and fitted with a fan and condensers: this was kept burning for three weeks continuously, during which time it was fed with sludge cake alone, and this sometimes contained more than 30 per cent of water, as some came straight from the press. The sludge gives ample heat for its own distillation, and might also be used to raise steam in the same furnace if desired.

The ammonia comes over with the liquor just as in gas

works, together with a quantity of light buttery tar which floats on the liquor. The cakes are reduced to a fine ash, which, if the temperature is raised by increasing the blast, can be changed into clinker. A very slight blast is sufficient to distil with, merely enough to get the products of distillation through the condensers.

Now the first question that will suggest itself is, What portion of the theoretical yield of ammonia is actually obtained?

Eighty per cent was what I actually obtained with the apparatus I had there, and it is at least probable that more could be obtained with better apparatus.

If the blast is carefully regulated the uncondensed gases will burn, being of similar composition to what is termed " producer gas "; this might be employed in raising steam to drive the fan, pumps, &c., working up the ammonia liquor or distilling the tar. I had originally intended to mix the ammonia, fixed as sulphate with the ash, to form a manure for general purposes; this cannot be done if there is much free lime in the ash, as ammonia is disengaged too readily.

Here perhaps I ought to state the reasons which compelled me to give up working at Leyton (where I was treated with great kindness by the authorities). The first reason was the low value of the ash, which contained about about 60 per cent of calcium salts. This great excess is due to the addition of lime first to precipitate and afterwards to press with.

The lime also introduces another difficulty, and that is the production of clinker in the furnace. The temperature of the furnace must of course be kept up to that point at which inflammable gas is produced, and when this is done it is hard to avoid a certain amount of clinker being formed also.

In the case of some towns where clinker can be used this might be done, and the ammonia alone relied on as a source of income, since sludge cake, even as produced at present, will yield enough ammonia to do more than pay for its distillation in the manner described.

The uncondensed gases from distilling or baking sludge cake have an exceedingly unpleasant smell, and must be burnt to avoid creating a nuisance.

Some time ago experiments were made of burning cake made from London sewage in a kind of oven, built with partitions so that the heat from one assists the one next to it, fires being lighted successively. The cake burnt without difficulty, but the ash being of little value it was abandoned. I believe no attempt was made to collect the ammonia.

A few years ago some ovens were tried at Leyton for burning the sludge cake to obtain ash; they either did not attempt or were unable to obtain the ammonia.

There was little or no sale for the ash, and it was subsequently abandoned.

III.

As regards a method of precipitation to go with the method of utilising sludge cake which I have just detailed :—

It is obvious where a separate system is used for storm water the ash will be worth more, as it will not be so contaminated with silica and other mineral substances from the roads.

Of course what is wanted is a means of producing a sludge cake as rich as possible in ammonia and phosphate, at the same time without adding precipitants in any large quantity which would lower the percentage of phosphate in the ash. At the same time the pressing ought to be done without lime; this is possible, as it is done at Kingston.

I have not been able to make experiments on this subject, but it seems certain that the use of lime ought to be avoided at all costs, and I should be inclined to try carbonised sludge in powder mixed with salts of alumina and iron, after precipitation running the liquid through a bed of lumps of carbonised sludge; when this bed is too foul to use any longer it can be burnt in the furnace.

I was not successful in preparing carbonised sludge in the same furnace that I have spoken of, though I think it could be done in a larger one. The attempt was made to rake out a portion of the sludge after being carbonised, but before it was burnt to ash. At any rate, if this cannot be done the cost of carbonising sludge in closed retorts heated by the inflammable gases I mentioned would not be prohibitive.

It seems probable that by using a sufficient quantity of this carbonaceous material (which can so readily be renewed) a considerable degree of purity could be arrived at in the effluent.

Any seeds present in the sludge, which are sometimes very numerous, are of course destroyed in the furnace and any vegetable matter reduced to ash, so that potash contained in the solids suspended in the sewage is rendered available.

As to what proportion the resulting manure if the whole of my scheme were in operation would be by weight to the cake dealt with, it is not possible to speak with accuracy—it might probably be one-tenth.

At the present day it is fast becoming widely felt that it is the duty of towns to treat their sewage in some way, so that no injury may be caused to health, yet we surely ought not to rest content with processes which yield nothing but refuse. It is now many years since Liebig insisted on the need of maintaining a proper circulation of phosphates and ammonia if we wish our land to remain fertile, and this need instead of diminishing shows itself more clearly every day.

ON THE NATURE OF SOLUTION.
No. IV.
By J. ALFRED WANKLYN and WILLIAM JOHNSTONE.

CONTINUING our work we are now prepared with a tabular statement of sulphates, and a table of alkalies, and a table containing ammoniacal salts and organic acids.

The figures tell their own tale, and require very little comment at this stage of the enquiry.

Certain ammoniacal salts show a minus value for $i - i_1$ that means that expansion takes place.

Ammoniacal Salts.

	Sp. gr.	i_1.	i.	$i-i_1$.
$(NH_4)_2OSO_3$	1·724	0·420	0·510	+0·090
NH_4NO_3..	1·691	0·402	0·384	−0·018
NH_4Cl	1·449	0·310	0·280	−0·030

Organic Acids.

Oxalic acid $C_2H_2O_4+2H_2O$.	1·436	0·303	0·330	+0·027
Tartaric acid $C_4H_6O_6$	1·739	0·425	0·460	+0·035
Citric acid $C_6H_8O_7+H_2O$ ..	1·515	0·340	0·372	+0·032
Succinic acid $C_4H_6O_4$	1·428	0·300	0·296	−0·004

Sulphate of Ammonia.

The specific gravity of the solid salt was found to be 1·724 at 20° C. A solution containing 25·00 grms. in 100 c.c. of the solution had specific gravity 1·127.

$$i = 0·510$$
$$i_1 = 0·420$$
$$\overline{0·090}$$

$$3(NH_4)OSO_3+2H_2O.$$

Nitrate of Ammonia.

The specific gravity of the solid salt was found to be 1·691. A solution containing 21·980 grms. n 100 c.c. of solution had specific gravity 1·0844.

$$i = 0·384$$
$$i_1 = 0·402$$
$$\overline{-0·018}$$

Chloride of Ammonium.

Specific gravity of the solid found, 1·449. A solution containing 10 grms. per 100 c.c. of the solution had specific gravity 1·028.

$$i = 0·280$$
$$i_1 = 0·310$$
$$\overline{-0·030}$$

Laboratory, Fish Street Hill, E.C.
September 1, 1891.

IMPROVEMENTS IN CHEMICAL MANIPULATION.
By H. N. WARREN, Research Analyst.

Production of Platinum Crucibles.

PERHAPS no other utensil is more often required in the laboratory where mineralogical determinations have to be made than platinum vessels of varying sizes. All that is required is to select a circular piece of platinum foil of the required size, fold it twice, the same as for a filter-paper, and a platinum crucible is at once formed that can be used with even greater advantage than an original and costly crucible, and which, after the fusion and extraction of the same has been performed, may be, if desired, reopened and used as ordinary foil.

Gold and Silver Crucibles made.

Select a porcelain crucible of convenient size, and apply to the outside of the same a solution of pyroxylin in ether, dry it by blowing for a few minutes upon the surface;

Sulphates.

	Specific gravity.	i_1.	i.	$i-i_1$.	
K_2OSO_3	2·63	0·620	0·784	0·164	$2K_2OSO_3+3H_2O.$
Na_2OSO_3	2·693	0·629	0·910	0·289	$2Na_2OSO_3+5H_2O.$
$CaOSO_3$	2·9	0·655	0·970	0·315	$2CaOSO_3+5H_2O.$
$MgOSO_3$	2·61	0·616	0·894	0·278	$MgOSO_3+2H_2O.$
$FeOSO_3$	2·62	0·618	0·975	0·357	$FeOSO_3+3H_2O.$
$CuOSO_3$	3·572	0·720	1·00	0·280	$2CuOSO_3+5H_2O.$
$ZnOSO_3$	3·40	0·706	0·952	0·246	$ZnOSO_3+2H_2O.$
NH_4OSO_3	1·724	0·420	0·510	0·090	$3(NH_4)_2OSO_3+2H_2O.$

Alkalies.

	Specific gravity.	i_1.	i.	$i-i_1$.	
LiHO	1·495	0·331	1·116	0·785	$LiHO+H_2O.$
NaHO	1·923	0·480	1·068	0·588	$4NaHO+5H_2O.$
KHO	2·00	0·500	0·841	0·341	$KHO+H_2O.$
CaH_2O_2	2·5	0·600	1·290	0·690	$CaH_2O_2+3H_2O.$
SrH_2O_2	4·0	0·750	1·230	0·480	$SrH_2O_2+3H_2O.$
BaH_2O_2	5·0	0·800	1·120	0·320	$BaH_2O_2+3H_2O.$

when dry, apply to the same either solution of argentic nitrate, as the case may be, or solution of auric chloride; suspend the same while still moist over a strong solution of sulphurous acid ; a sufficiency of gas will at once escape to give it a metallic coating : when this is accomplished connect the same to a battery of required strength, employing the usual depositing solution of either metal as desired. A compact metallic crucible, of varying thickness in accordance with the time allowed, is thus obtained ; the inner or porcelain crucible is now detached, by applying the flame from a Bunsen burner, the pyroxlin filim being thus destroyed, forming a space between the two, by which both are thus freed from each other.

Flasks coated with Metallic Copper.

The usual method of coating flasks, or other like articles, with metallic copper is very tedious, the first operation being to render the surface rough by means of fluorides, and afterwards applying plumbago to the prepared surface in order to obtain a conducting material upon which to obtain a deposit. All this preliminary, however, may be viewed as unscientific and waste of time ; all that is required is to generate, from a small hydrogen apparatus, a stream of antimony hydride, and allow the flame of the same to impinge upon the cold surface of the article in question. A deposit of metallic antimony is at once established, upon which a surface of metallic copper may be deposited by the usual method.

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ON THE DIRECT ABSORPTION OF AMMONIACAL SALTS BY CERTAIN PLANTS.

By A. B. GRIFFITHS, Ph.D., F.R.S.E., &c.

PROF. ACHILLE MÜNTZ (*Comptes Rendus*, vol. cix. ; *Journ. Pharm.* [5], vol. xx.) has recently shown that the roots and rootlets of certain plants* are capable of absorbing salts of ammonia without first being converted into nitrates.

At the time of Müntz's researches I forwarded him a letter (dated Nov. 20, 1889), detailing some experiments which I had performed on the same subject, and which entirely confirmed his researches. However, it may be stated that my experiments were performed in a different manner to those of Müntz.†
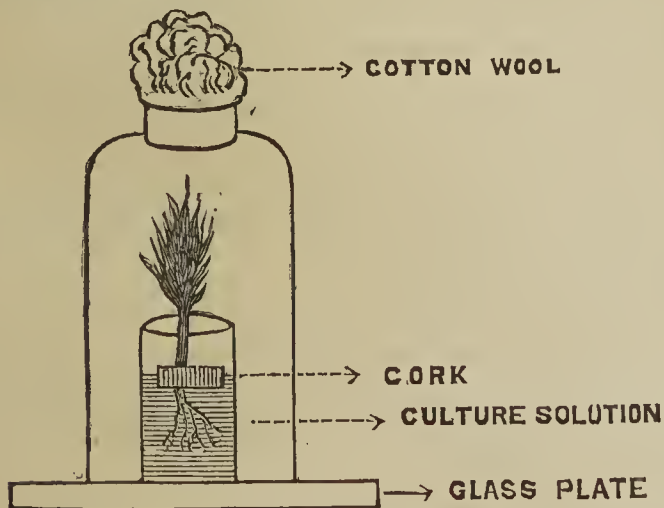
Concerning these experiments (which are detailed below) he wrote to me as follows :—" Je suis heureux d'apprendre que vos expériences conduisent au même résultat que les miennes, quoique conduites d'une

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* Beans, barley, hemp, and maize.
† Professor of Chemistry in the Institu National Agronomique, Paris.

manière différente. Votre méthode me semble tout à fait irréprochable et l'absorption directe des sels ammoniacaux, qui n'avait jamais été absolument démontrée, est aujourd'hui appuyée sur des preuves certaines."

These experiments were as follows :—

A large number of seedlings (beans) were immersed for thirty minutes in a solution of copper sulphate in order to destroy any nitrifying microbes present on the roots, stems, leaves, &c., of the young plants. After immersion the young plants were washed in sterilised distilled water, and the roots placed in sterilised culture solutions containing the following ingredients :*—

Distilled water	1000 c.c.
Potassium chloride	1·00 grm.
Ferrous carbonate	0·03 ,,
Sodium chloride	0·50 ,,
Calcium sulphate	0·50 ,,
Magnesium sulphate	0·50 ,,
Tricalcium phosphate	0·50 ,,
Ammonium sulphate	0·50 ,.

The plants grew in sterilised glass apparatuses (see fig.†) which only admitted sterilised air,—that is, air which had previously filtered through plugs of cotton-wool (sterilised). The plants grew remarkably well for four weeks, although the nitrogen in the culture solutions was only in the form of ammonium sulphate, and nitrification was prevented.

The culture solutions were tested afterwards for nitric nitrogen by the Schlœsing method (Griffiths' " Treatise on Manures," p. 362; Whittaker and Co.), but not the smallest trace of nitric nitrogen could be detected in the twenty-four separate culture solutions used in the experiments.

It may be stated that no nodules formed on the roots and rootlets of the bean plants during growth ; hence there was no direct absorption of atmospheric nitrogen.

The culture solutions each contained 0·05 per cent of ammonium sulphate ; but after the experiments this figure was reduced to 0·027 per cent.

It appears, from these experiments, that the nitrogen was absorbed as ammoniacal nitrogen by the roots of the plants, and not as nitric nitrogen ; for microbes were excluded, consequently nitrification was rendered impossible.

In conclusion, there appear to be three sources from which bean plants derive their supplies of nitrogen:—

(*a*). Nitrates in the soil (nitrification, &c.).
(*b*). Atmospheric nitrogen (by the aid of microbes).
(*c*). Ammoniacal salts.

If in nature the ammoniacal salts are, as a rule, first converted into nitrates, there can be no doubt that in certain cases they are also absorbed unchanged.

THE BACTERIOLOGICAL EXAMINATION OF WATER.

By Dr. G. FRANK.

THERE is no need of any further demonstration, that in order to decide on the suitability of a water for domestic and dietetic purposes its bacteriological examination is most prominently requisite. To fulfil this requirement in all cases has its peculiar difficulties.

For the purpose of chemical analysis a water may, without injury, be preserved for a considerable time, and hence it may be forwarded to an expert from a great distance, as the chemical properties of a sample of water change on keeping, only very slowly. With bacteria the case is very different.

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* All the salts used were chemically pure.
† The bell-glass and glass plate were first washed in a strong solution of mercuric chloride, dried, and then heated to 130° C. in a hot-air steriliser.

If water is preserved in bottles there occurs a very rapid multiplication of the bacteria present, so that in some cases their number, even in a few hours, is many times greater than the number found immediately after drawing the sample (Meade Bolton, " Behaviour of Various Bacteria in Drinking-Water," *Zeitschrift fur Hygiene*, vol. i., 76). As far as our present knowledge extends, this multiplication is not connected with the number and the kind of the bacteria originally present, with the chemical character of the water in question, or with external influences such as air and light, but it appears to us as purely arbitrary, *i.e.*, the conditions and laws of this increase are as yet little known. We are, therefore, by no means able, from the number of bacteria found in water a certain length of time after sampling, to calculate back to the number originally present. Some observers have selected the variety and number of the different species found in a sample of water which has been retained as a character whence the quality of the water might be inferred. If even any determination of species—saving the exceptional cases in which pathogenic bacteria were present in the water—is of subordinate importance as compared with a determination of the number of germs, it is in every case, when water has stood for some time, and an increase of germs has consequently taken place, absolutely worthless. We now know that probably all bacteria, with perhaps the single exception of the bacillus of tubercle, can multiply in water; but we do not know the rapidity of this multiplication in the different kinds. Further, if a water containing many various species is preserved for a considerable time, we invariably observe that with the increase of the number of germs the multiplicity of species diminishes, so that ultimately there remains only a single kind, whilst all the others had disappeared. Hence there has been formed by natural selection a pure culture of the species which can best maintain itself, and multiply under the prevailing circumstances. Hence, in the case of a water which has stood for a certain time, we cannot assume that all the species which were originally present will still be found at the time of our delayed investigation; on the contrary, we must keep in mind the fact that a portion of them, *i.e.*, those which increase more slowly, have already perished. Whether, therefore, in judging of a water we lay more weight upon the number of the germs or the multiplicity of the species, we must always be careful that no long time may elapse between the moment of cultivation and the installation of our culture-experiments.

In order to meet this demand, even in cases where a long time would pass between obtaining the sample and its arrival in the laboratory, the author has put together in a small box, all the apparatus which are absolutely necesssary for the bacteriological examination of water. After having satisfied himself by prolonged experience of the simple management of this set of apparatus, he has undertaken with its means to have the culture-experiments executed by persons who have not had a bacteriological training.

The apparatus consists of (1) four flat culture-vessels closed with cotton-wool, of the form indicated and used by Fodér, Soyka, and Roszahegyi ; (2) a tin capsule with six short pipettes for 1 c.c. ; (3) two bottles with well-fitting glass stoppers for taking the samples. All these utensils are sterilised and carefully packed in a small wooden box. This is then inserted in a larger wooden box, which in summer can be cooled with ice.

A.—*Requisites.*

The requisites are :—

1. The objects packed in the box.

(*a*) Four roundish bottles with flat sides, filled with nutrient gelatin (culture vessels); (*b*) a tin box with five pipettes ; (*c*) two small bottles with glass stoppers. The wadding plugs of the culture-vessels, the glass stoppers of the little bottles, and the lid of the tin box

must on no account be exposed to the air previous to actual use, or be drawn out of the necks of the bottles.

2. A washing dish with warm water at 35°. The temperature must be regulated by a thermometer.

The cultivation-vessels are plunged into this warm water so as to melt the gelatin. Particular care must be taken that the plugs of wadding are not moistened with the water.

3. A table or other horizontal support upon which the cultivation vessels are laid whilst the gelatin congeals.

4. Washing-water, soap, nail-brush, file for the nails, and clean towels.

5. In case of need crushed ice.

B.—*Conspectus of the Process.*

The entire operation resolves itself into :—

1. Liquefaction of the nutrient gelatin in the cultivation vessels by setting them in warm water.

2. Filling the small bottles with the water to be examined.

3. Taking a measured quantity of water out of the filled bottle by means of a sterilised pipette, mixing the water with the liquefied gelatin in the cultivation vessels, and stoppering the latter.

4. Letting the gelatin congeal.

5. Packing up the cultivation vessels.

C.—*General Rules and Preparatory Manipulations.*

1. In taking the sample of water for bacteriological examination, and in introducing the water into the cultivation-vessels, the most scrupulous cleanliness and the closest observation of the rules given are absolutely necessary.

2. For the experiment two persons are needed. One sees to the taking of the sample, and its introduction into the cultivation-vessels. The other undertakes to pump the water, or to purify the mouth of the pipe. He undertakes the liquefaction of the gelatin in the cultivation-vessels.

3. The water which has been stagnating in the pipes, or in the pump-well, must be removed before taking the samples of water. For this purpose, if the fittings are in perfect order, it is sufficient to let the water run out with the cock open to the full for ten minutes before taking the samples, or in the case to pump vigorously for the same length of time. But if visible impurities are detected at the overflow pipe they must be most carefully removed. In case of pumps the fittings must be in good condition.

4. The person who effects the sampling takes off his coat, turns up the sleeves of his shirt on both arms, and secures them so that they may not slip down accidentally. He then washes his hands and arms most carefully with soap and a brush up to over the elbow joint. Especial care must be taken in cleansing the finger nails, which are ultimately trimmed with the nail file. Finally the hands and arms are dried with a clean towel.

5. After both hands and arms are thus most thoroughly cleansed, one of the two small empty bottles is taken out of the box (which has been previously opened), in order to receive the sample.

N.B.—The second empty bottle serves as a reserve if the first has not been satisfactorily filled.

6. The bottle, still stoppered, is placed with one hand in the slowly-flowing stream of water. The stopper is then taken out with the other hand in the stream ; the bottle is filled and lastly the stopper is re-inserted, still in the current of water.

D.—*Charging the accompanying Cultivation-Vessels.*

1. The glass stopper of the bottle which has been filled is taken off and laid upon the table with its flat top downwards. One of the two pipettes in the box is taken out and plunged with its pointed end into the bottle down to the bottom.

2. The water is let rise freely into the pipette from below until it stands above the upper mark.

3. When the pipette is thus properly filled, its upper end is firmly closed with the tip of the right fore-finger and the pipette is thus lifted out of the bottle. The glass stopper is then inserted in its place.

4. By cautiously lifting the forefinger, so much water is allowed to flow out of the pipette, that the level of the water in the pipette may exactly reach the upper mark.

5. The operator now draws out the plug of wadding with his left hand by a rotatory motion from the neck of one of the cultivation vessels (which the assistant has previously heated until the gelatin is liquefied), and retains it in his left hand.

6. The point of the pipette containing water is now inserted into the neck of the cultivation-vessel, and the water is allowed to flow out of the pipette (by easing the pressure of the right forefinger), until its level has fallen to the lower mark.

7. When this has been done the cultivation-vessel is again closed with its plug of cotton-wool.

8. The water is mixed with the gelatin by repeatedly inclining the cultivation-vessel gently, and this vessel is then placed upon the above-mentioned horizontal support (A, 3) until the gelatin has congealed.

9. The other cultivation-vessels are then supplied with water in exactly the same manner, using each time a fresh pipette. They are then, after the gelatin has thoroughly "set," packed up in the box in exactly the same manner as when they arrived.

10. If an irregularity has occurred in any of these operations the fact must be noted on the accompanying label, indicating the cultivation-vessel, the filling of which has been thus interfered with.

E.—*Preservation, Packing, and Return of the Box.*

The box when received is to be kept in a cool, but dry place. For its return a time of despatch must be selected such that it may be detained as briefly as possible on the way. The time of sampling and filling the cultivation vessels must be chosen so that it may be sent off as directly afterwards as possible.

In hot weather the box is placed in a chest with a double lining of sheet-metal. The space between the two sides is filled in the case with pounded ice, and on its return the water must be poured off and a fresh supply of ice introduced.—*Zeit. fur Anal. Chemie*, xxx., p. 305.

CONTRIBUTIONS TO MICRO-CHEMICAL ANALYSIS.*

By H. BEHRENS.

(Continued from p. 124.)

XXXIV.—*Silicon.*

1. SODIUM salts precipitate from fluoriferous solutions of silicon hexagonal prisms; tables and stars of 40—70 micro., hexagonal rosettes of 80—140 micro., all distinguished by distinct outlines, and a peculiar pale rose-red colouration. Highly dilute solutions deposit during evaporation at the margin of the drop crystals chiefly prismatic. Limit of the reaction 0·00005 m.grm. Si.

For many silicates it is sufficient to heat the specimen gently with hydrochloric acid and ammonium fluoride, after which we may at once proceed to precipitation with sodium chloride. If potassium is present it separates out, before the addition of the sodium chloride, as potassium silico-fluoride in very pale cubes of 10—20 micro. Further, titanium, zirconium, tin, and boron yield with sodium fluorides which are very similar to the fluosilicate. The volatility of silicon tetrafluoride renders it possible to avoid these difficulties by distillation with ammonium fluoride and sulphuric acid. Water or ammonium acetate

* Zeit. Anal. Chemie.

serves for receiving the distillate. If the presence of boron is suspected it is necessary to fractionate at about 140°.

2. From acid solutions of molybdic acid which have been heated with soluble silica, rubidium chloride precipitates a yellow crystalline deposit of rubidium silico-molybdate. (Compare Rubidium 1.) The reaction is extremely sensitive, but caution is required in its use. Its limit is at 0·000004 m.grm. Si.

The solution is fused with five volumes of soda, dissolved in nitric acid, adding ammonium molybdate and a little rubidium chloride. If phosphoric acid is present there is a speedy separation of yellow phosphomolybdate; otherwise it is heated to about 70° in order to form phosphomolybdate. It is better in order to escape deception by arsenic or by the separation of pulverulent molybdic acid to heat the liquid and only to add rubidium chloride if no precipitate has been formed. It must also be remembered that glass is perceptibly attacked by heating with strong acids, and that besides arsenic, antimony, vanadium, niobium, tantalum, and bismuth, react with molybdic acid similarly to phosphorus, whilst thorium, zirconium, titanium, and tin form compounds similar to silico-molybdic acid, and may thus be confounded with silicon.

According to a process previously indicated by the author, the silica of silicates which are decomposed by hydrochloric acid may be detected in thin sections, dyeing with a watery solution of magenta. This process is not suitable for flocculent silicic acid, as the preparations would have to be washed with a large quantity of water. Not all decomposable silicates behave in the same manner with dyes. Malachite green seems to act better than magenta.

XXXV.—*Carbon.*

1. From soluble carbonates the carbonic acid may be precipitated by salts of calcium, lead, or strontium. The finely pulverulent precipitate of calcium carbonate changes in a short time to small, well-formed rhombohedra. Lead carbonate crystallises more quickly in rods and lenticles of 15 micro.

Graphite and coal can be made fit for examination by combustion with 10 parts by bulk of saltpetre. As, notwithstanding all care, potassium nitrite is formed, salts of lead are here not applicable. Strontium nitrate reacts almost as quickly. Strontium carbonate forms globules of 6—12 micro. (Compare Strontium 4.) If pyrites are present salts of calcium must be used. Limit of the reaction 0·001 m.grm. C.

2. From insoluble carbonates the carbonic acid is expelled by strong acids in the form of a gas. The specimen is placed in a drop of water under a covering glass, a drop of hydrochloric acid is placed at its margin, and the water is absorbed at the opposite side with a slip of filter paper. Upon thin sections there are obtained both greater sensitiveness and localisation of the reaction. The latter may be increased as follows :—The specimen is covered with a solution of glycerin and gelatin in water, the layer is allowed to congeal and covered again after about 10 per cent of diluted hydrochloric acid has been added to the mixture.

XXXVI.—*Boron.*

1. In solutions of boric acid in hydrofluoric acid, or in hydrochloric acid and ammonium fluoride, potassium salts produce pale rhombs of 77°, or on slowly cooling, six or eight-sided tables and ridges, which are rather better defined. If the crystals are too pale they may be improved by re-crystallisation from hot water. Silicon, if it interferes, can be expelled by evaporation before the addition of potassium chloride, or by precipitation with barium chloride. Limit of reaction 0·0002 m.grm. B.

2. Ammonium fluosilicate, if sublimed with boriferous substances, yields fluoborate, which is treated as in 1. Limit at 0·0004 m.grm. B.

XXXVII.—*Aluminium.*

In solutions of aluminium sulphate which are not too dilute, salts of cæsium produce the formation of well-developed colourless octahedra of cæsium alum which measure 40—90 micro. Solutions containing more than 1 per cent aluminium sulphate yield dendritic structures, solutions with less than 0·2 per cent do not readily yield good octahedra.

If cæsium chloride is used the solution of the sulphate must contain a little free sulphuric acid, but a large excess is injurious. Iron has no influence on the reaction. Limit at 0·00035 m.grm. Al.

2. Ammonium fluoride precipitates from neutral or slightly acid solutions of aluminium salts, pale, well-developed octahedra of 20—60 micro., soluble in nitric acid, but reproduced by ammonium acetate. The ammonium fluoride must be used in considerable excess, the solution of aluminium must contain no sodium and no iron. This reaction is equal in sensitiveness to the former, but it bears more dilution.

Aluminium hydroxide can be detected by means of dye wares. A watery solution of Congo-red is very serviceable. Care must be taken that the precipitate adheres firmly to the glass, so that the coloured preparation may be left in water for an hour.

XXXVIII.—*Iron.*

1. Potassium ferrocyanide gives a blue flocculent precipitate, the colour of which is distinctly perceptible under a magnifying power of 200 diameters. The limit of visibility is at the 5000th dilution of the iron salt, hence the limit of the reaction is 0·00007 m.grm. Fe. A large excess of strong acids must be avoided, as they can form Prussian blue from the reagent.

2. Ammonium fluoride preipitates ferric salts in the same manner as aluminium salts. The crystalline octahedra are colourless, with rather stronger margins than the crystals of the aluminium compound. The precipitation with ammonium fluoride is of more value for iron than for aluminium, as the iron in the crystals, after rinsing once with water, may be easily shown by means of ammonia. Conversion into Prussian blue does not give a good result. Limit of the reaction at 0·0002 m.grm. Fe.

3. Barium chloride and oxalic acid give in solutions of ferric chloride, instead of the short rods of barium oxalate, curved, curly, light brown hairs of 300 micro. in length. An excess of the reagents must be avoided. Limit of the reaction 0·0001 m.grm. Fe. Here also the behaviour of aluminium is similar, causing the formation of colourless tufts. The iron compound is coloured brown by ammonia and blue by potassium ferrocyanide.

XXXIX.—*Chromium.*

1. Silver nitrate, notwithstanding its rather lower sensitiveness, deserves the preference to lead salts, on account of the tendency of silver chromate to separate out from slightly acid solutions in large, characteristic crystals, which can be easily recognised along with precipitates of chloride, vanadate, &c. Concerning its properties see Silver 2. The limit of the reaction is at 0·000025 m.grm. Cr.

2. On lead chromate—compare Lead 4. It is difficult to obtain crystals, and the yellow colour of the finely granular precipitate, which appears only by reflected light, is readily overlooked. The limit of the reaction is at 0·00002 m.grm. Cr. Salts of chrome are preferably oxidised to chromates by fusion with saltpetre and soda, but in this manner the degree of sensitiveness mentioned above cannot be reached. The mean result was 0·0056 m.grm. Cr.

XL.—*Vanadium.*

1. Ammonium chloride added in excess to alkaline solutions of vanadic acid precipitates ammonium meta-vanadate in colourless lenticular crystals of 12—20 micro.

They polarise strongly with right extinction. Limit of the reaction 0·0003 m.grm. V.

2. Silver nitrate gives in solutions of vanadates acidulated with acetic acid a yellow precipitate, which, on heating with dilute acetic acid, are converted into orange rods of 10 micro. Limit of reaction 0·00007 m.grm. V.

XLI.—*Niobium.*

1. Soda-lye precipitates from alkaline solutions of niobic acid, and from solutions of the fluorine salts of fluorine, the salt $NaNbO_3 + 3H_2O$ in the form of colourless rods of 20—30 micro. They often coalesce in stellar groups, which may be mistaken for sodium tantalate. Hot water partially decomposes sodium niobate; it can be re-crystallised in free alkali. It is sparingly soluble in concentrated soda lye. The limit of the reaction is at 0·0006 m.grm. Nb.

2. The orange-red colour of niobic acid with tincture of galls and hydrochloric acid is of no value for the diagnosis of niobic and tantalic acid.

(To be continued).

DETERMINATION OF THE FINAL POINT IN THE TITRATION OF ZINC BY MEANS OF POTASSIUM FERROCYANIDE IN AN AMMONIACAL SOLUTION.*

By F. MOLDENHAUER.

THE author uses as indicator a 4 per cent solution of copper sulphate, with which he moistens a slip of very white and smooth filter-paper, 5 c.m. in breadth, in the following manner:— He draws a narrow longitudinal streak along the filter-paper by means of a hair-pencil saturated with the copper solution, and dries it quickly over a flame. Cross sections of this slip, of 2 to 4 m.m. in breadth, are cut off and enclosed in a stoppered bottle. For use, a drop of the precipitated solution of zinc is let fall upon the white end of such a slip. The liquid, in consequence of the capillarity of the paper, quickly travels to the blue part and soaks into it. If a small excess of ferrocyanide is present, there appears on the blue boundary line a red or reddish streak, the intensity of which increases with the quantity of the fluid that traverses the paper. If the excess is very slight, the reddish colour does not appear immediately. It appears, however, quickly and certainly if there is an excess of 0·1 to 0·2 c.c. of a decinormal solution of ferrocyanide in 100 c.c. of ammoniacal water. The appearance of the red streak is perceived the more easily the lighter is the laboratory, the whiter the paper and the background,— *e.g.*, white porcelain. Recently prepared paper is more sensitive than such as has become old, but the latter becomes sensitive again in a moist atmosphere containing acetic acid. Good lamp-light, with a screen of opal glass, does not interfere with the detection of the reaction.

The titration may be performed either in heat or in cold. The author generally operates in heat.

The strength of the solution of ferrocyanide is so adjusted that 1 c.c. corresponds to 0·005 grm. zinc. The stœchiometrical relation requires 16·2615 grms. ferro-ferrocyanide to 1 litre. If the standard of the solution is checked with potassium-zinc sulphate it is always found a little too strong, whence the author uses the factor 1·01 in order to calculate the c.c. used, which exactly corresponds to 0·005 grm. zinc.

Potassium ferrocyanide at the dilution employed for titrating zinc is at first almost colourless. Very soon, however, it turns of a gold-yellow, and if kept for a long time it deposits a slight quantity of ferric oxide. This

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* *Chemiker Zeitung* and *Zeit. Anal. Chemie*

change is avoided by adding 1 to 2 grms. of caustic potassa to 1 litre of the solution, and preserving it in bottles of a dark colour.

The titration of zinc is interfered with slightly by the presence of much ferric oxide, but considerably by manganese and magnesia.

In the latter case the author employs the following process :—He dissolves 2·5 grms. of ore in hydrochloric acid, and dilutes without filtration to 250 c.c. An efflux burette is rinsed twice or three times with about 5 c.c. of this solution, 60 c.c. are poured into the burette, and 50 c.c. are then run out into a small flask. To this quantity there are then added 10 c.c. ammonia and 5 c.c. of a solution of ammonium carbonate, containing, in 100 c.c., 5 grms. solid ammonium carbonate, 5 grms. salammoniac, and 10 c.c. ammonia. It is heated until a dense precipitate subsides, and is set aside to cool. In the meantime the efflux burette is again filled with the original solution, 25 c.c. are poured into a beaker along with 10 c.c. ammonia, and the consumption of ferrocyanide is determined to 1 c.c.; 25 c.c. more of the original solution are added, and the mixture is titrated accurately. If the final point is exceeded, a few drops of the solution of the ore are again added, and the final reaction is once more produced, noting the quantities consumed of both solutions.

In the meantime the contents of the flask first mentioned will have cooled sufficiently. To the ammoniacal solution there are added 1 or at most 2 c.c. of a 10 per cent ammoniacal solution of sodium phosphate. The whole is shaken up for a short time and is then titrated, —that is after all manganese and magnesia present have been eliminated. If both are not present the result will agree with that first obtained, otherwise the latter result must be accepted as correct.

Before the experiment is regarded as decisive it is well, after a short time, to ascertain whether the final reaction is permanent ; in some cases a few more tenths of a c.c. of the ferrocyanide solution must be added.

Manganese also can be titrated by means of ferrocyanide if no other bodies are present which are precipitated by the same reagent. To this end a measured quantity of a decinormal solution of potassium ferrocyanide is mixed with sal-ammoniac and ammonia, and the faintly acid or neutral solution, manganous solution, is dropped into the solution of ferrocyanide until the reaction on the slip of copper-paper just ceases to appear.

NOTICES OF BOOKS.

Gas-Works Statistics, 1891. Edited by CHARLES W. HASTINGS. London : Hazell, Watson, and Viney.

IN the production and sale of gas no very important changes have been made. The gas varies very widely both in illuminating power and in price. In the former respect Milnthorpe takes the lead with a power of 23. Southport makes gas at 21·5, and Liverpool at 21·25. Thrale is near the bottom of the scale with 12-candle gas, for which it contrives to obtain 6s. 8d. per 1000. The prices of gas in different towns seem to have little relation either to the local cost of coal or to the scale of the operations. We notice two towns, Mottram and Mossley, both situate near to coal-mines and both having railway communication ; yet Mottram vends 10-candle gas at 6s. 3d., whilst Mossley produces 19¼-candle gas for 3s. The information supplied by the gas producers is more complete than that furnished by the water undertakings.

In the illuminating power of gas Scotland still takes the lead. That of Banchory has 33-candle power ; Colinsburgh, made from oil, 65 ; Eyemouth and Tain, each 32 ; whilst upwards of twenty towns supply a 30-candle gas. The lowest quality we find is that of Dollar, 22-candle ; that of Glasgow is 33.

The highest quality made in Ireland is that of Larne, 22 candle. The poorest Irish gas is that of Magherafelt, 12-candle.

In Wales, Amlwch takes the lead with 23-candle gas, but elsewhere the highest standard reached is 19-candle.

A very useful feature, which might be obtained from the corporation and local boards, would be the maximum limit of sulphur permitted.

The Gas and Water Companies' Directory, 1891. Edited by CHARLES W. HASTINGS. London : Hazell, Watson, and Viney, Limited.

THIS publication, which has now reached its fifteenth year, has a distinct field from its companions, the Gas and Water Works Statistics. It gives, in parallel columns, the name of each town concerned, the date of formation of the gas or water undertaking, the special Acts (if any), total share capital, dividends, total loan capital ; names of chairman, manager, and secretary ; population, distance from London, and railway by which the town is reached. In the many cases in which the undertakings are the property, not of a company, but of the rate-payers, some of these items are necessarily absent. The dividends seem in many cases exorbitant for undertakings which are sure of a constant demand, and which cannot be troubled with bad debts, dead stock, or changes of fashion. The corporations which own gas or water works, or both, number 159, whilst 85 local boards are in the same position.

A new feature is a directory of electric-light installations, showing the capital invested, the system, capacity, price per unit, name of electrician in charge, and the area of supply.

The reader may be surprised to find that some of the most important and energetic cities, such as Birmingham, Leeds, and Manchester, have not adopted the new source of light.

An appendix gives the amount of local taxation paid by the gas and water installations.

Attempt at a Theory of the Sun and of the Variable Stars. (Essai d'une Théorie du Soleil et des Etoiles Variables.) By A. BRESTER, Jun., Sc.D. Delft : J. Waltman.

THE author ascribes all the phenomena of sun and the variable stars to a single cause—the intermittent chemical combination at the (comparatively) cool exterior of matter which had previously dissociated by heat. He regards the sun as displaying the stratified structure which gravitation gave it at the time of its formation. It is characterised by its imposing tranquillity. The protuberances which are regarded as the effects of terrible perturbing currents have in reality deceptive appearances, and are merely transitory lights.

The Foundations of Chemistry. (Grundlagen der Chemie.) By D. MENDELEEFF, Professor at the University of St. Petersburg. Part 6. St. Petersburg : Carl Ricker.

THIS part continues the study of the reputed elements, from mercury, including the bodies of the 3rd, 4th, and 5th groups as far as antimony. At the close of the 16th chapter the author suggests that his predicted element, eka-cadmium, may possibly be the " Norwegium " which Dahll discovered in the island of Krageiö. He considers, however, that further investigation is here necessary. Mention is here also made of Phipson's " Actinium " (1881), concerning which, however, nothing has been heard since 1882.

The origin of the vapours which issue from the earth charged with boric acid is pronounced for the present inexplicable, pending more general researches.

In the section on aluminium we find analyses of four Russian soils, in none of which do we find any alumina

mentioned as present! The celebrated "black earth" from the province of Simbirsk is given as containing, in 10,000 parts of the air-dried sample,—

Na_2O	11
K_2O	58
MgO	92
CaO	134
P_2O_5	7
N	44
S	13
Fe_2O_3	341

The characteristic of this soil seems to be the large proportion of ferric oxide. The other three soils—described respectively as clayey, sandy, and peaty—are also not said to contain any alumina. We can only suspect here a clerical or typographical error.

The author adopts as convenient Graham's terms "hydrogel" for gelatinous hydrates, and "hydrosol" for soluble hydrates. He shows that compounds of alumina, &c., with bases, are evidently, like solutions and alloys, determined by similarity, and form a transition from mixtures to the type of the true salts.

We find it mentioned that alunite like that of La Tolfa occurs in large masses in Transcaucasia.

The author is of opinion that the method of Ste.-Claire Deville is still the most advantageous for the production of aluminium and its alloys.

Concerning the detection and separation of the rare earths we find no new information. The method of Crookes — the examination of the electro-phosphores-cent spectra of the earths in high vacua — is substantially pronounced too sensitive, as being affected by the minutest admixture of the oxides. The recently discovered elements of didymium — *e.g.*, Welsbach's neodymium and praseodymium—are regarded as possibly mixtures.

The observations of Graham (1861—1864), on the transformations which the soluble and the gelatinous forms of silica respectively undergo, are pronounced as ranking among the most important steps towards an explanation of the formation of organic structures.

A passage occurring as a footnote at the end of the 16th chapter merits especial notice. The author writes: —"I consider it is suitable here to make mention of the absence of an element between cadmium and mercury. But as not one element is known in the 9th series of the periodic system, it is possible that only elements belong to this system which are *not capable of existence.*" Not capable of existence on our globe, but perhaps possible in other heavenly bodies ? This we submit is an extraordinary passage to have proceeded from the pen of a chemist who does not recognise the evolution of the elements as possible.

CORRESPONDENCE.

AN EXAMINATION MUDDLE.

To the Editor of the Chemical News.

SIR,—The Science and Art Department, in the recent examination in Honours Practical Chemistry, gave a brass wire in which students were told to estimate the quantity of copper, an outline of the process to be followed being given. It seems, however, that this work was beyond the scope of the Syllabus, and, in many cases, beyond the capabilities of the students. The wire contained about 65 per cent of copper, and the results varied from 20 to 90 per cent, and many students never made an estimation at all.

Owing to the remonstrance of teachers and students, who protested against anything not in the Syllabus being given, the examination seems to have been decided on the results of the qualitative analysis alone, and we have the curious spectacle of students about 40 per cent out in a copper estimation passing in "Honours," and consequently certified as *qualified* to teach chemistry including quantitative analysis.

The examination in Honours must consequently have been easier than that of the Advanced Stage, which, in addition to a similar qualitative analysis, includes a written paper of questions.

Two of my own students (one in Honours and the other in the Advanced Stage) got exactly the same qualitative work, and both did it correctly. The Honours student, however, did not make his quantitative analysis, and the other seems to have been very weak in his answers to the paper of questions. The result of the examination is that the Honours student has obtained a second class, while, in the lower or Advanced Stage, the student who *did exactly the same work has failed.*

The facts are admitted by the Department, who, however, do not seem to see any absurdity in the same work passing one student in the higher and failing another in a lower stage.

Whatever value that might have been attached to the Honours certificate has surely been lowered by this action of the Department, and an injustice done to students who have obtained their certificates in former years.—I am, &c.,

TEACHER.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxiii., No. 9, August 31, 1891.

This issue does not contain any chemical matter.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. vi., No. 2.

On the Use of Ammonium Sulphoselenite for Distinguishing the Alkaloids.—Prof. Ferreira da Silva. —This paper will be inserted in full.

A New Procedure for Extracting the Colouring-Matter of Natural Wines.—Louis Hugounenq.—The author uses the reagent of Roos, a solution of tartaric acid at 1/10, which is neutralised with a slight excess of ammonia and mixed with neutral lead acetate, until the lead precipitate ceases to dissolve. It is allowed to settle and filtered ; the reagent is then poured into wine neutralised with ammonia as long as a precipitate is formed. This precipitate, collected and washed, is suspended in a small quantity of alcohol at 80°. Dilute sulphuric acid (about 15 per cent) is then added, avoiding excess. The liquid takes an intense red colour, and lead sulphate is precipitated and filtered off after standing for some hours. The alcoholic filtrate is mixed with 20 vols. of pure water. Almost all the colouring-matter is immediately precipitated. It is collected, washed, and dried at a low temperature. It is purified by re-dissolving it in alcohol and evaporating the solution *in vacuo* over sulphuric acid. The method may be successfully applied for extracting the colouring-matter of lyes.

On Diethylamidocaproic Acid.—E. Duvillier.—The copper salt of this acid corresponds to the formula, $C_{20}H_{40}N_2CuO_4$. The free acid is obtained by treating the copper salt with sulphuretted hydrogen and allowing the solution to crystallise.

On Hydroxanthranol.—C. E. Lineberger.—Levi and Bach, on causing benzyl bromide to react upon the reduc-

tion products obtained by means of zinc powder in an alkaline solution, obtained benzyloxanthranol. If the chloride is used instead of the bromide we obtain a body containing two hydroxyles, and corresponding to a term of reduction of anthraquinone which has not been previously prepared.

The Oxidation of the Azo-Compounds. — Ch. Lauth.—The author's experiments furnish a means of distinguishing the azo-compounds by their transformation into diazos, which under the influence of suitable reagents yield colouring-matters. The distinctness and rapidity of this reaction may be used analytically, and yield also a rapid means of obtaining the quinones in a state of purity.

Apparatus for Luminous Projection applicable to Balances of Precision in order to obtain Rapid Weighings.—A. Collot, Jun.—This paper requires the accompanying illustration.

Series 3, Vol. vi., No. 3.

Constitution of Caprylic Aldehyd.—A. Béhal.—Caprylic aldehyd is certainly, as generally admitted, at present normal methylhexylcetone.

Action of Benzyl Chloride upon Ortho- and Para-Toluidines.—Ch. Rabant.—An account of the sulphonic derivative of benzylorthotoluidine, of benzylparatoluidine, and of benzoylbenzylparatoluidine.

Action of Light upon Silver Chloride.—M. Guntz.—The substance of this paper has been already noticed.

Observations on a Memoir by Mr. Richards.—M. Guntz.—A controversy arising out of a paper contributed by Mr. Richards to the *Journal of the Franklin Institute*.

The Precipitation of Copper by Iron and the Action of Metallic Iron upon the Solutions of the Ferric Salts.—J. Ch. Essner.—Burnt copper pyrites, if alternately moistened and dried in the air, and afterwards exhausted with water yield a solution containing copper sulphate and ferric salts. If these solutions are treated with metallic iron at 70—80°, we obtain a deposit of metallic copper contaminated with a mud which is not easily removed. This mud was exclusively formed of ferric hydroxide. The copper, according to the quality of the iron employed, appears either as dust, as grains, or as fibres.

On the Composition of Certain Subterraneous Waters near Port Vendres, and on the Circumstances which Favour this Composition. — Ch. Essner.—The water in question contains free sulphuric acid, and attacks boiler plates to a dangerous extent. They are obtained from rocks containing pyrites and basic iron sulphates.

Researches on the Aromatic Oxyacetones.—P. Crepieux. — This memoir does not admit of useful abstraction.

Reactions of Xylose and Arabinose.—M. Tollens.—Referring to M. Bertrand's communications on the coloured reactions of xylose with orcine and phloroglucine (*Bulletin Soc. Chimique*, v., part 12), the author shows that Bertrand has been anticipated by Whuler, Allen, and Tollens, in the *Annalen der Chemie*, vol. ccliv., p. 314.

MISCELLANEOUS.

Spurious Coffee.—At Lille a manufactory of spurious coffee has been detected, and four of the offenders are in custody. The raw material consisted of the following articles:—15 kilos. chicory, 35 kilos. flour, and 500 grms. iron sulphate—the last mentioned ingredient serving to imitate the natural colour. The lustre of the berries was produced by means of an oil. The plant and materials have been confiscated.—*Chemiker Zeitung*.

The Invertebrata.—Messrs. L. Reeve and Co. have in preparation a volume entitled, "The Physiology of the Invertebrata," by Dr. A. B. Griffiths, F.R.S.E., F.C.S., &c. The book (illustrated with 81 woodcuts) will be of use to physiological chemists, as it treats of the applications of chemistry and physics to the solution of biological problems.

Method of Rendering Portland Cement Unattackable by Frost.—M. Reinhofer.—The object may be effected by the addition of a quantity of soda crystals dissolved in water. The mortar submitted to experiment was composed of 1 litre Portland cement, 1 litre of lime, 3 litres of river sand, mixed with a solution of 1 kilo. soda in 3 litres water. This mortar was exposed for $14\frac{1}{2}$ hours to a maximum cold of $-31\cdot5°$, and was then introduced for three hours into a furnace. When taken out its setting was found quite unaffected.—*Revista di Artiglieria e Genio*.

Alkali-Makers' Pocket-Book.—A new edition, revised and enlarged, of Professor Dr. Lunge and Dr. Hurter's "Alkali-Makers' Pocket-Book" will be issued in a few days in Messrs. Whittaker's Specialist's Series. In this edition numerous small errors in the first edition, almost unavoidable in such a case, have been corrected, some minor improvements have been made, and a considerable number of new methods for analysis have been introduced. The new table of specific gravities of sulphuric, hydrochloric, and nitric acid, and of liquor ammonia, constructed with extreme care, have been substituted for the tables of Kolb and Carius contained in the first edition. As the size of the page has been somewhat increased, the designation "handbook" has been substituted for "pocket-book."

The Chemical Laboratory of Wiesbaden.—In the Summer Term, 1891, there were 74 students on the books. Of these 60 were from Germany, 4 from Russia, 2 from North America, 2 from Spain, 1 from Austria, 1 from Luxemburg, 1 from France, 1 from Sweden, 1 from Bulgaria, and 1 from Australia. Besides the Director, Geh. Hofrath Prof. Dr. R. Fresenius, there are engaged as teachers in the establishment Prof. Dr. H. Fresenius, Prof. Dr. E. Borgmann, Dr. W. Fresenius, Dr. E. Hintz, Dr. med. G. Frank, and architect T. Brahm. The assistants in the instruction laboratory are 3 in number, in the private laboratory 17, and in the Versuchsstation 3. The next Winter Term begins on the 15th of October. Besides the scientific researches a great number of analyses were undertaken in the different departments of the laboratory and in the Versuchsstation during last term on behalf of manufacture, trade, mining, agriculture, and hygiene.

NOTES AND QUERIES.

Thermo-Chemistry.—Can any of your readers inform me through your paper as to the best and most recent work on Thermo-chemistry, publisher, and price.—C. B.

THE CHEMICAL NEWS.

VOL. LXIV., No. 1661.

THE SPONTANEOUS IGNITION OF COAL.*

By Prof. VIVIAN B. LEWES, Royal Naval College.

THE researches of Grundmann, Fleck, and Richters, on the Continent, have done much towards explaining the somewhat complex phenomena occurring when newly won coal is exposed to atmospheric influences; but in this country little attention has been given to the subject, and with the exception of a report by Sir Frederick Abel, and the late Dr. Percy in 1875, and which is buried in a Blue-book, as far as I know nothing has been published on the subject, with the result that the almost universally accepted explanation of the spontaneous ignition of coal is that it is due to the presence in it of iron pyrites, a theory which I think is entirely erroneous; and my excuse for bringing this paper before you is the enormous importance of the subject to one of the chief coal-producing districts in the kingdom.

The origin and formation of coal has long since been satisfactorily explained, and we know that coal is a fossil fuel of purely vegetable origin, and may look upon it as consisting of three distinct parts:—(1) carbon; (2) hydrocarbons, *i.e.* compounds of hydrogen with carbon, and also with traces of oxygen and nitrogen; and (3) mineral impurities, either derived from the sap of the original plants, which by their checked decay formed the coalmeasures, or else which have filtered into the coal during its formation from the surrounding soil.

Of these three factors it is the carbon which forms the bulk of the coal, and which during combustion gives the chief portion of the heat which is evolved, whilst the hydrocarbons, as soon as the coal is heated, escape as gaseous products, and give the fuel the power of burning with flame, and it is upon the proportions in which these principal constituents of the coal are present that the characteristic properties of the various varieties of coal, to a great extent, depend; for instance, in a good Welsh anthracite the percentage of carbon is very high, whilst the amount of volatile hydrocarbons is very low, with the result that the anthracite is hard to kindle and burns almost without flame, whilst a marked contrast to this is a good Cannel, or even Wallsend, coal, in which the percentage of carbon is considerably smaller, but in which the percentage of hydrocarbons is very high, with the result that such coals easily ignite and burn with a considerable amount of flame, or can be utilised for the production of coal gas.

The mineral substances, which are practically the impurities in the coal and mainly form the ash left after combustion, consist of sulphate of lime (gypsum), alumina, silica, and disulphide of iron pyrites, which latter forms the so-called coal brasses found in most seams to a greater or less extent.

Ever since Berzelius first expressed the opinion that the heat given out by the oxidation of iron disulphide into sulphates of iron might have an important bearing on the heating and ignition of coal, it has been adopted as the popular explanation of that phenomenon; and although the work of Dr. Richters clearly proves this not to be the case, the old explanation is still given,—a notable exception, however, being in the case of our great metallurgist, Dr. Percy, who, as early as 1864, pointed out that probably oxidation of the coal had also something to do with spontaneous combustion, a prediction

* Abstract of a Paper read before the British Association, Cardiff Meeting, 1891, Section B.

amply verified by Dr. Richters's researches some six years later.

This disulphide of iron is found in coal in several different forms, sometimes as a dark powder distributed throughout the mass of the coal, and scarcely to be distinguished from coal itself. In larger quantities it is often found forming thin golden-looking layers in the cleavage of the coal, whilst it sometimes occurs as large masses and veins, often an inch to two inches in thickness; but inasmuch as these masses of pyrites are very heavy, they rarely find their way into the screened coal for shipment, many hundreds of tons of these "brasses" being annually picked out from the coal at the pit's mouth and utilised in various manufacturing processes. If the air is dry the pyrites undergo but little change at ordinary temperatures, but in moist air they rapidly oxidise when in a finely divided condition.

It is during this process of oxidation that the heat supposed to cause the ignition is evolved. But when it is considered that some of the coals most prone to spontaneous combustion contain only eight-tenths of a per cent of iron pyrites, and rarely more than 2 per cent, the absurdity of imagining this to be the only cause of ignition becomes manifest. If 100 lbs. of coal were taken, and the whole of the pyrites in it concentrated in one spot, and rapidly oxidised to sulphate, the temperature would barely be raised to 100° C. if all loss of heat could be avoided. Besides which in certain manufactures pure iron pyrites are largely used, and when free from carbonaceous matter may be kept in a state approaching to powder, in heaps containing many hundred tons; and although undergoing continual oxidation, I have been unable to trace a single case of heating, much less a rise of temperature which would approach the igniting point of coal. When, however, it is mixed with finely divided carbonaceous matter, then heating and ignition is a frequent occurrence in even moderate-sized heaps.

I have carefully determined the igniting point of various kinds of coal, and find that—

Cannel coal ignites at	698° F.	=	370°	C.
Hartlepool coal	„ 766	„	= 408	„
Lignite	„ 842	„	= 450	„
Welsh steam coal	„ 870·5	„	= 477	„

So that no stretch of imagination could endow the small trace of pyrites scattered through a large mass of coal and undergoing slow oxidation, with the power of reaching the needful temperature.

From these considerations it is evident that we must unhesitatingly discard the old explanation of the cause of spontaneous ignition, and see what other factors we have to deal with.

Carbon, which constitutes so large a proportion of coal, is one of those bodies which possess to an extraordinary degree the power of attracting and condensing gases upon their surface, this power varying with the state of division and density of the particular form used. The charcoal obtained from dense forms of wood, such as box, exhibits this property to a high degree, whilst certain kinds of coal also exhibit the same power, although to a less extent. The absorptive power of newly won coal due to this surface attraction varies, but the least absorbent will take up $1\frac{1}{4}$ times its own volume of oxygen, whilst in some coals more than three times their volume of the gas is absorbed. This absorption is very rapid at first, but gradually decreases, and is, moreover, influenced very much by temperature, for reasons which will be explained later, and this absorption itself causes a rise in temperature which aids the action that is taking place.

The rate of absorption varies with the amount of surface exposed, and therefore able to take part in the condensing action, so that when coal or charcoal is finely powdered, the exposed surface being much greater, absorption becomes more rapid, and rise of temperature at once takes place.

If charcoal is kept for a day after it has been made, out

of contact with air, and is then ground down to a powder, it will frequently fire after exposure to the air for thirty-eight hours; whilst a heap of charcoal powder, of 100 bushels or more, will always ignite. It is for this reason that, in making the charcoal for gunpowder, it is always kept after burning, for three or four days in air-tight cylinders before picking over, and ten days to a fortnight before it is ground.

If newly won coal be at once placed in a measured volume of oxygen, the gas is at first absorbed and its volume diminished; but after it has been in the gas for some little time the coal commences to give off carbon dioxide, and careful investigations show that the oxygen first taken in by the absorptive power of the carbon is now entering into chemical combination with the hydrocarbons of the coal, combining with the hydrogen to produce water, and with the carbon to form carbon dioxide, whilst a small proportion remains in combination in the coal itself, so that the action taking place is of two kinds,—first, absorption of oxygen; and secondly, the setting up of chemical action between the absorbed oxygen and the hydrocarbon.

The absorption of oxygen gives rise to heat, and in the case of coal this rise in temperature all tends to increase the rate of the action which is going on; but it is rarely sufficient to bring about spontaneous ignition, as only about one-third the amount of oxygen being absorbed by the coal,—that is, is taken up by the charcoal, and the action being much slower,—tends to prevent the temperature reaching the high ignition point of the coal. Air-dry coal absorbs oxygen more quickly than wet coal. The oxygen so absorbed is in a chemically more active condition than when present in the air, as, in the first place, it is in a condensed condition, and, secondly, is diluted with less nitrogen than in the air, as the carbon absorbs a higher proportion of oxygen than of nitrogen, and this oxygen so absorbed rapidly commences to attack the hydrocarbons present in the coal, having apparently but little action on the carbon itself.

During this action the hydrogen of the hydrocarbons unites with the oxygen to form water, which mostly escapes as vapour, whilst the carbon unites with oxygen to form carbon dioxide or carbonic acid gas, and both these actions result in the generation of heat, which under ordinary circumstances is dissipated to surrounding bodies, but which, when generated in the centre of a mass of fine coal—which, owing to the fact that its interstices are filled with air, is an admirable non-conductor of heat—causes a rise of temperature which in turn increases the rate of action and generation of heat, until a temperature is reached at which the so-called spontaneous ignition ensues.

The most important point to be noticed is the extraordinary effect which initial temperature has on the rapidity of chemical actions of this kind. At a low temperature, and indeed up to about 100° F. = 38° C. the absorption of oxygen, and consequent chemical action, will go on slowly, with practically little or no chance of undue heating taking place; but directly the temperature exceeds 100° F., then, with some classes of coal, ignition is only a question of time and mass.

Although the ignition point of various coals lies above 700° F., yet if many of these coals are powdered, and are placed in perforated zinc cases in masses of 2 lbs. or upwards, and these are kept at a steady temperature of about 250° F. in an oven, ignition will generally follow in a few hours, whilst between this and 150° F. it will take days instead of hours for the same result to follow, and at ordinary English temperatures the mass of broken coal must be very great before much risk of ignition is incurred.

In a paper which I read before the Institution of Naval Architects in 1889 I pointed out that, in the case of coal cargoes, the influence of temperature and mass could be easily traced, and that liability to spontaneous ignition increases with—

1. The increase in the bulk of the cargoes. Evidence given before the Royal Commission of 1875 showed that, in cargoes for shipments to places beyond Europe, the cases reported amount to ¼ per cent in cargoes under 500 tons; in cargoes from 500 to 1000, 1 per cent; 1000 to 1500, to 3·5 per cent; 1500 to 2000, to 4·5 per cent; and over 2000 tons, to no less than 9 per cent. Mass influences this action in two ways:—

(a.) The larger the cargo the more non-conducting material will there be between the spot at which heating is taking place and the cooling influence of the outer air.

(b.) The larger the cargo the greater will be the breaking-down action of the impact of coal coming down the shoot upon the portions first loaded into the ship and the larger thereby the fresh surface exposed to the action of the air.

2. The ports to which shipments are made (26,631 shipments to European ports in 1873, resulting in only ten casualties, whilst 4485 shipments to Asia, Africa, and America, gave no less than sixty).—This startling result is partly due to the length of time the cargo is in the vessel, the absorption and oxidation being a comparatively long action; but a far more active cause is the increase of temperature in the tropics, which converts slow action into a rapid one.

3. The kind of coal of which the cargo consists (some coals being specially liable to spontaneous heating and ignition).—There is great diversity of opinion on this point, but it is pretty generally admitted that cases of heating and ignition are more frequent in coals shipped from east coast ports than in South Wales shipments. So much, however, depends upon the quantity of small coal present, that a well-loaded cargo of any coal would be safer than a cargo of Welsh steam coal in which a quantity of dust had been produced during loading.

4. The size of the coal (small coal being much more liable to spontaneous ignition than large).—This is due to the increase of active absorbent surface exposed to the air,—a fact which is verified by the experience of large consumers of coal on land—gas managers recognising the fact that coal which has been stamped down or shaken down during storage is more liable to heat than if it had been more tenderly handled, the extra breakage causing the extra risk.

5. Shipping coal rich in pyrites (or brasses) whilst wet.—The effect of external wetting on coal is to retard at first the absorption of oxygen and so to check the action; but it also increases the rate of oxidation of the pyrites, and they, when oxidised, swell and split the coal into pieces, and this increases heating due to the exposure of fresh dry surfaces, and it is practically only in this way that the presence of pyrites tends to increase the list of spontaneous ignitions.

6. Ventilation of the cargo.—For ventilation to do any good, cool air would have to sweep continuously and freely through every part of the cargo,—a condition impossible to obtain in coal cargoes, whilst anything short of that only increases the danger, ordinary methods of ventilation supplying just about the right amount of air to create the maximum amount of heating. The reason of this is clear. A steam coal absorbs about twice its own volume of oxygen, and takes about ten days to do it under favourable conditions, and it is this oxygen which, in the next phase of the action, enters into chemical combination and causes serious heating. Ventilation, such as used to be sometimes arranged for by a box shaft along the keelson with Venetian lattice up-shafts, supplies about as much air as is necessary to produce the results which end in spontaneous ignition.

7. Rise in temperature in steam colliers, due to the introduction of triple expansion engines and high-pressure boilers.—The increase in stokehold temperature due to this is from 5—10° F., and this affects the temperature of the adjacent parts of the vessel.

The same factors which tend to give rise to spontaneous

ignition in coal cargoes will also be found to be the chief causes of ignition in large masses of coal ashore, and the most prolific source of fire in big stores of coal at gas-works, &c., is to be found in ventilating shafts improperly applied, breaking up of the coal, or in some accidental rise in initial temperature, such as a steam-pipe or a boiler in contact with a wall against which the coal is stored.

In the case of coal bunkers in modern steamers and war-ships, the conditions under which the coal is placed are so totally different from those existing in a collier that no comparison can be drawn between them.

In the coal bunker the question of mass, which plays so important a part in a hold laden with coal, is almost entirely eliminated, as 50—400 tons would be about the capacity of any ordinary bunker, and it has been before shown that the cases of spontaneous ignition in masses of coal less than 500 tons does not amount to more than ¼ per cent, and the question of initial temperature becomes the most important factor.

A few years ago such an occurrence as a coal bunker on fire was rare, whilst at the present time hardly a week passes without some more or less serious cases occurring on the fast liners, and it is evident that there must exist some well-defined cause for this enormous increase in cases of spontaneous ignition. On collecting evidence on this point, the first thing that strikes one is that bunker fires are almost entirely confined to vessels in which the bunker bulkheads are only separated from the funnel by a narrow air space, or are in close proximity to the boilers themselves, but where the bunkers are stepped back from the funnel casing and boilers, spontaneous ignition is a great rarity.

Taking the case of a fast liner, it is found that the temperature in a coal bunker varies very considerably, according to its proximity to the air channel round the funnel casing. Close to the outside of the bulkhead the temperature is often as high as 200° F. = 93° C., whilst inside 120° would be a fair estimate, and from the centre of the bunker to the side of the vessel it is seldom above 75° F. = 24° C., the temperature, however, being higher nearer the iron decks, which, being in contact with the heated bulkhead, conduct the heat through the coal and raise the temperature often up to 100° F.

It has been pointed out that if coal is kept at a high temperature, even though it be far below its igniting point, ignition is only a question of time, and if the bunker coal next the bulkhead is kept at 120° F. any coal with a tendency to absorb oxygen will run a great chance of igniting within a few days. It is manifest that if this is the real cause of ignition, the seat of the fire ought to be found close to the heated bulkhead, but this is very often not the case, the mass of fire being found near the centre of the bunker, and sometimes even towards the side of the vessel; but careful examination soon reveals the cause of this, as a line of charred coal is mostly to be found running from the heated bulkhead to the seat of active combustion, showing that the fire started by the high initial temperature has not had sufficient air near the bulkhead to do more than smoulder, but that as soon as it came in contact with a current of air passing up through the coal from the hatches in the decks the smouldering mass began to burn fiercely.

The tendency to spontaneous ignition in coal has always been supposed to increase with the quantity of pyrites present in it, but experiment shows that it is the tendency or power of the coal to absorb oxygen which must be taken as the true index of danger, and this may be roughly guaged by the amount of moisture which the coal has absorbed from the air, as if much moisture be found in an air-dried sample of coal it at once stamps it as a highly-absorbent form, and which must on that account be stored with special precautions, whilst if but little moisture be present it is probably unable to take up enough oxygen to lead to serious mischief.

This is very beautifully shown in a table compiled, I believe, by Dr. Percy, which also makes it clear how little the pyrites have to do with ignition :—

Liability to spontaneous combustion.	Pyrites p.c.	Moisture p.c.
Very slight	1·13	2·54
	1·01 to 3·04	2·75
	1·51	3·90
Medium	1·20	4·50
	1·08	4·55
	1·15	4·75
Great	1·12	4·85
	0·83	5·30
	0·84	5·52
	1·00	9·01

When once a coal has taken up oxygen, and the early stages of heating are passed and the temperature has again fallen, all danger of ignition is over, and it may be stored in any quantity with perfect safety, so that if it were practical to keep newly-won coal for a month in moderate sized heaps, and then to avoid much breakage in afterwards loading it, spontaneous ignition would be almost unknown.

NOTE ON THE
ELECTROLYSIS OF ALLOYS.*

By HENRY C. JENKINS, Assoc.M.Inst.C.E., F.C.S.

THE importance of the question as to whether alloys are capable of being electrolysed has for a long time been recognised, and has already been under the notice of a Committee of this Association. Several experimenters have endeavoured to separate the constituents of some alloys by such means, but hitherto no success in this direction has been recorded.

Doubtless one reason for this negative result may be found in the difficulty of submitting a metallic bath to a sufficiently large difference of potential, owing to its very low resistance, but from the same cause there is another reason why electrolysis should not take place, at least in the case of the majority of alloys, to which prominence does not hitherto seem to have been given.

The variable polarisation, and the resistance of electrolytic baths generally, have led to the adoption of the view that, in an electrolytic bath, the electricity is conveyed by some method of convection, or of successive molecular discharge; streams or chains of molecules carrying electrical charges from one electrode to the other. The bath itself is formed of some body whose resistance when pure is extremely high, so that it is necessary in general to add another body to it—an impurity—which probably acts by increasing the number of free molecules present. It is easy to imagine that in such an insulating medium molecules can be charged with electricity, which charge they can retain until they reach some body having a different potential. But free molecules could not retain a charge if entirely within a conducting envelope and in contact with it, and although the possibility of the possession of a gaseous envelope by the molecules in a liquid has been recognised, still the conductivity of pure molten metals is scarcely in favour of any view that there is actual insulation between their molecules, and if there were any considerable insulation of this kind, it is difficult to account for the effect upon electrolytes of very small electromotive forces. It will thus be seen that the want of success in the attempts to electrolyse molten alloys still leaves quite open the question of their constitution, whilst it is in full accordance with Laplace's equation of electrical potential.

From the fact, however, that alloys in many cases form

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* A Paper read before the British Association, Cardiff Meeting, 1891, Section B.

true compounds, which may be obtained in a crystalline form if proper conditions are chosen, and because the conditions as to temperature of an electrolytic bath may be those most favourable to the precipitation of such a compound out of solution, it follows that all future electrolytic experiments with alloys should be made at temperatures sufficiently high to fuse any possible compound, otherwise very deceptive results would be obtained, owing to the difficulty of correctly sampling the bath.

PRELIMINARY NOTE ON
TRAUBE'S TETROXIDE OF SULPHUR.

By DOUGLAS CARNEGIE, M.A.

IN the current number of the *Berichte* (June 8) Traube, in a paper on the so-called persulphuric acid (obtained by electrolysing 40 per cent solutions of sulphuric acid), quotes analyses which in his opinion prove that this substance is not S_2O_7, as its discoverer (Berthelot) supposed, but that it is in reality the radicle sulphion SO_4.

Although the author sees no theoretical objection to the existence of a peroxide of sulphur of the composition SO_4, yet he does not think that Traube's analyses are such as to warrant a dogmatic assertion to the effect that such an oxide is known and realisable.

It is the object of this paper to criticise Traube's methods and conclusions.

In the first place it should be noted that Traube did not succeed in isolating his alleged SO_4. His conclusions are founded on analyses of solutions of the peroxide of sulphur in (I.) H_3SO_4Aq, and (II.) K_2SO_4Aq.

I. A portion of the persulphuric acid solution was treated with excess of ferrous sulphate, and then the excess of ferrous iron titrated with permanganate. In this way the "active" oxygen of the peroxide was determined. From another portion of the boiled acid solution $BaSO_4$ was precipitated, by means of $HClAq$ and $BaCl_2Aq$. The weight of this precipitate gave the amount of SO_3 resulting from the complete decomposition of the peroxide.

TABLE I.

Active O found.	BaSO₄ found.	SO₃ calculated.	Ratio O : SO₃.
9·62 m.g.	144 m·g.	49·5 m·g.	1 : 5·14

Theory for $SO_4 — SO_3 : O :: 5 : 1$.
     „ $S_2O_7 — SO_3 : O :: 10 : 1$.

From a comparison of the theoretical and experimental numbers Traube concludes, firstly, that Berthelot's oxide cannot be S_2O_7; and secondly, that it must have the composition SO_4. (It may be noted, in passing, that in spite of the speciousness of the ratio 1 : 5·14 the experimental results nevertheless involve an error of 2·8 per cent, if Traube's views be correct.)

While admitting the justness and necessity of the first conclusion, I nevertheless hesitate to accept the second, and for the following reasons:— Moissan, from determinations of total hydrogen and active oxygen, concludes that the so-called perchromic acid has the empiric formula $CrO_3.H_2O_2$. From certain considerations founded on the formula for hydrogen peroxide, taken in conjunction with Mendeleeff's "principle of substitution," it would, however, seem better to double Moissan's empiric formula, and write it in the form $Cr_2O_7.H_2O_2.H_2O$. Such a formula is supported by the well-known fact that peroxides (as defined by Mendeleeff, *Berichte*, xv., 242) possess a remarkable power of combining with H_2O_2 to form fairly stable compounds. Whether or not Fairley's peruranates will, on the more detailed investigation which they undoubtedly deserve, turn out to be similar derivatives of the oxide U_2O_7, as Mendeleeff suggested in his Faraday lecture, remains to be seen. Quite recently compounds

of the peroxide form M_2O_7 (where M = W and Mo) have been described, so it would seem that all the members of the sulphur group—as group is understood in connexion with the periodic law—form oxides of the type M_2O_7.

Now there is nothing whatever in Traube's analyses to show that he was not working with the very probable compound $S_2O_7.H_2O_2xH_2O$, which would on decomposition furnish SO_3 and active O in the proportion 5 : 1. As a matter of fact the conditions observed in the preparation of Berthelot's oxide would be favourable to the production of hydrogen peroxide, and, moreover, Traube himself states that the sulphur oxide under discussion is decomposed by pure water, with formation of hydrogen peroxide and evolution of oxygen.

It cannot, however, be claimed that this reaction of the peroxide with water has much weight as an argument for the proposed formula $S_2O_7H_2O_2$. For that anomaly, potassium peroxide, K_2O_4, is said to be decomposed by water, with production of hydrogen peroxide and oxygen.

II. The primarily obtained solution of sulphur peroxide in electrolysed H_2SO_4 was exactly neutralised by $KOHAq$. Thus there resulted a solution of the peroxide (itself wholly destitute of acidic properties) in neutral K_2SO_4Aq.

The active oxygen in a portion of this neutral solution was determined ferrometrically as in I., and also iodometrically. Another portion of the solution having been boiled, the SO_3 resulting from the decomposition of the alleged SO_4 was determined by standard alkali. In this way the following numbers were obtained :—

TABLE II.

Active Oxygen determined Ferrometrically. M.grms.	Active Oxygen determined Iodometrically. M.grms.	SO₃ determined Acidimetrically. M.grms.	Oxygen (Iodometric): SO₃.
8·40	7·28	36·4	1 : 5·00
6·06	5·04	23·0	1 : 4·56
16·20	12·00	56·2	1 : 4·70
27·15	21·28	110·3	1 : 5·10
32·00	24·00	117·0	1 : 4·89
		Mean	1 : 4·85

It will be noticed that the iodometric determinations of active oxygen always fall below the ferrometric ones. Traube advances the following explanation :—The potash used to neutralise the solvent H_2SO_4 contained carbonated alkali ; hence the resulting neutral solution would contain, besides the peroxide and K_2SO_4, considerable quantities of potassium bicarbonate. This bicarbonate, Traube asserts, would react with an *equivalent quantity* of the iodine set free, and so vitiate the final thiosulphate titration. Even admitting what seems improbable, viz., that the neutralised solution contained considerable quantities of $KHCO_3$, can we further permit ourselves to agree with Traube in his assertion that bicarbonate fixes an equivalent quantity of iodine? Fresenius, in his "Quantitative Analysis," quotes special experiments showing that aqueous solutions of the bicarbonated alkalies are practically without action on iodine.

According to Traube the presence of this bicarbonate also vitiates the SO_3 determinations, but in such a way that the error tends to compensate that made in the iodometric determinations. Hence the ratio O : SO_3 is unaffected by the double error.

We find ourselves unable to appreciate the portion of Traube's paper following the above discussion of the iodometric error. Suppose the ratio $\frac{a}{b}$ to have a certain value, K, and let x be any quantity. Then it is obvious mathematically that the ratio—

$$\frac{a + x}{b + \dfrac{x}{K}}$$

will have the value K. Nevertheless Traube would see in this numerical discovery a strong confirmation of the existence of the compound SO_4.

Final experiments are then described which do away with the disturbing influences supposed to be caused by the presence of bicarbonates. At the same time these experiments render possible the direct determination of the ratio $SO_3 : O$ determined ferrometrically. I have supplemented the results given in Table III. by a column of percentage errors.

TABLE III.

Active Oxygen determined Ferrometrically.	SO_3.	$O : SO_3$.	Percentage Errors.
22·54 m.grm.	96·3 m.grm.	1 : 4·3	14·5
23·90 ,,	108·6 ,,	1 : 4·5	9·2

Errors of 14·5 and 9·2 per cent do not appear to embarrass the ardent seeker after SO_4. Traube, commenting on the above results, concludes—" Here also the ratio of both decomposition products *is nearly* 1 : 5 (*sic*). There is no doubt but that an indifferent body of the composition SO_4 exists."

In a previous paper which appeared in this Journal I showed that the unreliability of Duflos's method of estimating ferric salts is referable to the impurity of ordinary samples of " pure " KI, which salt invariably contains more or less free alkali. To the same source I would in part refer the discrepancies between the iodometric and ferrometric oxygen determinations alluded to. Some of the iodine set free in the reaction—

$$S_2O_7H_2O_2 + 4KI = 2K_2SO_4 + H_2O + 2I_2$$
$$[\text{or } SO_4 + 2KI = K_2SO_4 + I_2 \text{ (Traube)}]$$
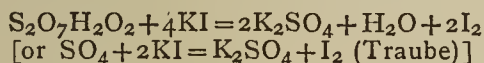
reacts at once with an equivalent of the potash presumably contained as impurity in the potassium iodide used, and vitiates the results. Hence it is reasonable to suppose that the iodometric method would give true values for the active oxygen were acid, instead of neutral, solutions of the peroxide employed. In a footnote Traube asserts that this is actually the case.

It has previously been remarked that the conditions observed in the preparation of sulphur peroxide are eminently favourable to the production of H_2O_2. It may be that more of this substance is formed than is necessary to combine with the S_2O_7 produced to form $S_2O_7H_2O_2$; at any rate the low ratio $O : SO_3$, found in the majority of Traube's analyses seems to demand some explanation other than mere experimental error. Moreover, in neutral solutions the reaction—

$$H_2O_2 + 2KI = 2KOH + I_2$$
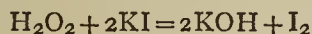
would not take place quantitatively, and herein one may seek for a further explanation of the discrepancies between the iodometric and ferrometric determinations of active oxygen, and of the fact apparent in Table II., that the iodometric error increases *pari passu* with the quantity of peroxide analysed.

The greatest discrepancy between the ferrometric and iodometric oxygen determinations quoted in Table II. amounts to 8 m.grms. oxygen. It is easy to see that 56 m.grms. of free alkali in the KI used would produce an error of this magnitude. If 3 grms., say, of potassium iodide were used in the volumetric determination, a potash impurity of less than 2 per cent—by no means an excessive quantity—would fully account for their regularities noticed.

The foregoing criticism of Traube's work suggests several experiments on the peroxide of sulphur, and these I hope to carry out and communicate shortly.

Boulder, Colorado

Intermittent Mercurial Air-Pump. — K. Prytz (*Annalen der Physik*).—A wide U-tube with limbs of unequal length. If mercury is let fall with a certain speed into the longer limb, a certain quantity of mercury is each time expelled from the oblique end of the shorter limb into the descending tube.

CONTRIBUTIONS TO MICRO-CHEMICAL ANALYSIS.*

By H. BEHRENS.

(Continued from p. 150).

XLII.—*Tantalum.*

1. SALTS of potassium produce in solutions of tantalic and hydrofluoric acids the separation of thin prismatic crystals of the sparingly soluble salt K_2TaFl_7, whilst fluoxyniobate, which is formed simultaneously, remains in solution. The prisms of potassium fluotantalate resemble crystals of gypsum; their length amounts to 50—100 micro. The limit of the reaction is at 0·006 m.grm. Ta.

The required solution is most simply obtained by melting tantaliferous minerals with sodium and ammonium fluoride. It is dissolved in hot water with the addition of a little hydrochloric acid. It is preferable first to separate out a mixture of tantalic and niobic acids by fusion with potassium bisulphate and extraction with hot water, and to bring this into solution by heating with water and ammonium fluoride, adding finally a little hydrochloric acid. For a tolerably complete precipitation of tantalum, at least ten minutes must be allowed after the addition of the potassium chloride.

2. Soda-lye precipitates from alkaline solutions of tantalic acid the salt $Na_4Ta_6O_{19} + 25H_2O$ in hexagonal tablets and stars measuring 30—50 micro. They are colourless, and otherwise they resemble the crystals of sodium silico-fluoride. At the beginning of the crystallisation there appear also rods and needles which can scarcely be distinguished from crystals of sodium niobate. On this account the reaction 1 deserves the preference. The limit is at 0·0012 m.grm. Ta.

XLIII.—*Bismuth.*

1. Oxalic acid throws down from solutions of bismuth a heavy, pulverulent white precipitate. The precipitation is effected more rapidly and completely by means of potassium bioxalate. If heated in the acid liquid bismuth oxalate crystallises in pyramids of a quadratic section which refract light strongly and are from 6—15 micro. in size. The limit of this reaction which ensues decidedly at a dilution of 1000 times is at 0·0003 m.grm. Bi.

2. Rubidium chloride and cæsium chloride yield with compounds of bismuth dissolved in hydrochloric acid, hexagonal tables probably belonging to the rhombic system, which are 300 micro. in size with rubidium chloride and 100 micro. with cæsium chloride. They are thin, but have a well-defined outline and polarise strongly. If tin is present bismuth falls subsequently in prismatic crystals extended in length. For solutions which contain less than 0·2 per cent of bismuth nitrate, cæsium chloride is preferable as a reagent. An addition of potassium iodide retards the reaction and makes the crystals smaller. They appear as ridges, rhombs, and hexagons, varying from the colour of red lead to blood red. This reaction, which attaches itself conveniently to the examination of tin, indicates 0·00013 m.grm. Bi.

3. Potassium sulphate (or preferably bisulphate), yields colourless discs in solutions of bismuth if not too dilute (compare Potassium 3). They are more easily found than the small pyramids of reaction 1, but the reaction with potassium sulphate requires solutions which contain at least 0·2 per cent of bismuth nitrate. Limit of the reaction 0·0003 m.grm. Bi.

4. The precipitation of bismuth nitrate or chloride by water cannot be recommended for micro-chemical research. Much more striking phenomena are obtained by an addition of potassium iodide. From a hydrochloric solution water precipitates bismuth iodide with a blackish brown colour, which turns to a reddish brown on heating;

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* *Zeit. Anal. Chemie.*

in presence of lead it is scarlet, of antimony dark red, and of tin orange-red. Limit of the reaction 0·0004 m.grm. Bi.

XLIV.—*Antimony.*

1. In solutions of antimony chloride in dilute hydrochloric acid cæsium chloride produces crystals of about 80 micro. very similar to those described under Bismuth 2. Rubidium chloride yields crystalline leaflets of 300 micro. paler than those of chlorobismuthite. If potassium iodide is added along with cæsium chloride, the sensitiveness of the reaction is doubled, and we obtain crystalline leaflets of a bright orange, the colour of which may be recognised along with bismuth, as iodostibite crystallises after iodobismuthite. The limit of the reaction is at 0·00008 m.grm. Sb.

2. Oxalic acid converts antimony oxychloride into antimonyloxalate. This compound is precipitated from slightly acid solutions of antimony by potassium bioxalate. It appears in translucent brownish tufts and pencils composed of very fine fibres. The oxalate dissolves in hydrochloric acid, but water re-precipitates it unaltered. These reactions may be masked by tin, bismuth, and lead. The limit is at 0·001 m.grm. Sb.

3. Barium tartrate with a slight addition of barium chloride dissolves at a boiling heat antimony hydroxide and oxychloride. Whilst cooling there are formed the crystalline leaflets of barium stibiotartrate described under Barium 4. If the antimony is previously eliminated as sulphide, as Streng recommends, the reaction is trustworthy and characteristic. It is then, however, more tedious than 1, and is about equal in sensitiveness to 2.

4. Precipitation as sodium antimoniate gives better results for antimony than for sodium. The specimen is melted with 5 vols. of saltpetre until about the half is driven off, dissolved in hot water, and to the clear solution there is added a granule of sodium chloride. The crystals obtained are chiefly lenticular, of 20—25 micro., often grouped in triplets, and intersecting each other according to the axes of an octahedron. Between them there occur little rods which might be taken for crystals of sodium niobate. The limit of this reaction is at 0·0005 m.grm. Sb. Hitherto it is the only available reaction for antimonic acid.

XLV.—*Arsenic.*

(*a*) Arsenious Acid.

1. Nitric acid produces no precipitate in a solution of arsenteroxide in potassa-lye unless highly concentrated. Evaporation at a gentle heat determines the separation of arsenious acid in small, distinct octahedra, the number and size of which increase whilst the liquid cools. They measure 8—15 micro., and refract light strongly and are colourless. Hydrogen sulphide turns them slowly yellow. The limit of the reaction is at 0·0002 m.grm., $As_2O_3 =$ 0·00014 m.grm. As.

(*b*) Arsenic Acid.

1. With the salts of calcium we obtain, by the same process as for the precipitation of ammonium magnesium phosphate, hemimorphous crystals of the rhombic system, up to 60 micro., and of the same appearance as those of the salt above mentioned.

From very dilute solutions we obtain chiefly small rods of 15 micro., in which the hemimorphic structures can scarcely be recognised. The limit of this very characteristic and sensitive reaction is 0·000035 m.grm. As.

The oxidation of arsenical compounds to arsenic pentoxide is best effected by gently heating along with hydrochloric acid and potassium chlorate. For the reaction just described it must be remembered that ammonium chloride dissolves perceptible quantities of ammonium-calcium arseniate. Arsenic acid forms analogous sparingly soluble double salts with zinc, cadmium, and copper, but not with strontium, barium, and lead.

2. Ammonium molybdate precipitates solutions of arseniates in dilute nitric acid at the ordinary temperature, but only after the lapse of some time. Heat accelerates the precipitation remarkably. The precipitate is perfectly similar to the ammonium phosphomolybdate. Limit of the reaction 0·00022 m.grm. As.

In all cases where supersaturation with ammonia is admissible, the preference must be given to reaction 1, which leaves no room for confounding arsenic and phosphorus. Besides, the reaction with molybdate admits of mistakes with vanadium and bismuth, and if much ammonium chloride is present in solution with silicon. Compare silicon and rubidium.

(To be continued).

NEW METHOD OF DETERMINING CHROME YELLOWS.

By MM. LACHAUD and C. LEPIERRE.

OUR researches on chromates have led us to propose a new process for the determination of lead chromate in the chrome yellows of commerce. Lead chromate, in contact with dilute solutions of potassa, is split up according to the equation—

$$2PbCrO_4 + 2KOH = PbCrO_4.PbO + K_2CrO_4 + H_2O.$$

If we precipitate the potassium solution by a strong and concentrated acid, the inverse reaction is produced and the lead chromate is regenerated. On the contrary, under certain conditions, the determination of the potassa which remains free in contact with basic chromate (which is almost insoluble if we operate in the cold and in a dilute liquid), furnishes a rapid process for the determination of lead chromates. According to the above equation 1 mol. lead chromate (323) corresponds to 1 mol. potassium hydrate (56), or 1 part of chromate to 0·17337 potassa.

We proceed as follows :—We weigh accurately 2 grms. lead chromate and prepare two solutions, one of binormal potassa (112 grms. KOH per litre); this potassa neutralises exactly a solution of sulphuric acid at 1 mol.-grm. per litre (98 grms.). The chromate is placed in a flask with a ground glass stopper, and there are added 20 c.c. of the standard potassa. It is shaken strongly until the yellow granules of the chromate disappear, and basic chromate occupies the bottom of the flask. The liquid is diluted with distilled water; it is decanted and filtered to separate the basic chromate. The excess of potassa is neutralised with the standard sulphuric acid, using phenol-phthalein as indicator. To render the process capable of determining the impurities in the chromates down to less than 1 per cent (which is sufficient in practice), we neutralise the larger part of the potassa with a certain volume of the binormal sulphuric acid, and we complete the titration with a solution of exactly the strength of this binormal solution; with 2 grms. of chromate and 20 c.c. of potassa, we add to the dilute liquid immediately 16 c.c. of binormal SO_4H_2. An excess of potassa is necessary to attack the chromate, for this renders the operation more rapid. If the solutions are ready prepared, and without counting the time of weighing, a chromate may be determined in ten minutes; this lapse of time is much less than that required by other volumetric methods.

But we may dispense with the filtration if many determinations have to be effected by making a small correction (scarcely 0·1 in 20 c.m.c.), due to the action of acid solutions upon the basic chromate. To render the operation more rapid by dispensing with calculations, we use a solution of potassa such that 0·1 c.m.c. corresponds to 1 per cent of pure lead chromate. For this purpose it is sufficient to prepare either with the normal solution or directly a potassic liquid containing 17·337 grms. of KOH in a litre of water, and to prepare a sulphuric solution neutralising it exactly; 1 litre of these two solutions corresponds to 100 grms. of pure chromate.

We weigh 2 grms. of chromate, and operate upon 40 c.c. of the potassa solution. If the chromate is pure, 20 c.c. of sulphuric acid are required to neutralise the potassa. If the chromate contains 50 per cent of impurities, 30 c.c. are required, &c.—*Bulletin de la Soc. Chimique de Paris.*

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING AUGUST 31ST, 1891.

By WILLIAM CROOKES, F.R.S.;

WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford;

and C. MEYMOTT TIDY, M.B., F.C.S., Barrister-at-Law, Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, Metropolis Water Act, 1871.

London, September 9th, 1891.

SIR,—We submit herewith the results of our analyses of the 174 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from August 1st to August 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 174 samples examined, the whole were found to be clear, bright, and efficiently filtered, excepting three, which were recorded as "very slightly turbid."

Throughout the month of August, notwithstanding the excessive and often stormy rainfall, the character of the water-supply to the Metropolis continued to be eminently satisfactory. The extreme degree of freedom from organic matter which characterised the supply of the previous month was fully maintained; and the effect of the storm-rainfall was noticeable only in a slightly diminished degree of freedom from colour-tint, and in the occurrence of the three samples of water noted as "very slightly turbid." The maximum amount of organic carbon present in any single sample examined was only 0·128 in 100,000 parts of the water, corresponding to considerably under a quarter of a grain of organic matter per gallon. A comparison of the results afforded by the Thames-derived supply in the months of July and August respectively, with the mean results afforded by the previous four months' supply, is shown in the following table :—

	Ratio of brown to blue tint.	Oxygen required for oxidation.	Organic carbon per 100,000	Organic carbon per 100,000
	Means.	Means.	Means.	Maxima.
Thames supply :—				
Mean of previous four months ..	13·0 : 20	0·051	0·147	0·209
July	8·9 : 20	0·046	0·121	0·142
August ..	11·4 : 20	0·045	0·114	0·128

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
WILLIAM ODLING.
C. MEYMOTT TIDY.

NOTE ON THE

COMPOSITION OF THE ASH OF THE ACHYRANTHES ASPERA, LINN.

By C. J. H. WARDEN,
Chemical Examiner to the Government of Bengal.

THE *Achyranthes aspera*—"prickly chaff flower"—occurs in India as a weed in gardens, and is found all over the country. In Sanskrit the plant is called Apàmárga, or the *washerman*, on account of the large quantity of alkali contained in its ash, which is utilised by native washermen in certain parts of India, and which is also used as an alkali in dyeing and in the preparation of alkaline medicines and caustic pastes.[*]

The plants used for the following ash determinations were collected in Alipore, Calcutta, in August. The leaves, stems, and roots, dried at 100° C., afforded respectively the following percentages of ash :—Leaves 24·334, stems 8·672, roots 8·863.

The ash had the following percentage composition :—

	Leaves.	Stems.	Roots.
P_2O_5	3·0257	2·6939	1·8594
SiO_2 as sand	39·7192	12·9716	21·4219
SO_3	1·3200	2·6534	3·9523
CaO	13·8893	13·1233	12·9335
MgO	3·4778	3·5149	5·4419
K_2O	17·8454	32·0008	28·5830
Na_2O	—	—	0·9860
Fe_2O_3	2·7931	3·0352	5·6297
Manganese (traces) ..	Not estimated.	Not estimated.	Not estimated.
KCl	5·7416	9·5221	—
NaCl	1·1770	1·5261	3·2951
Al_2O_3	2·0651	Not estimated.	Not estimated.
CO_2	8·8687	13·6294	11·0057
Charcoal	0·3297	0·5525	Not estimated.
	100·2526	95·2232	95·1085

The large amount of sand present in the ash was due to the plants having been collected during the "rains," and when received they were coated with finely-divided silicious matter—especially the leaves—which it was impossible to wholly separate. The total potash, if calculated as K_2O, would be equivalent in the leaves to 21·4986 per cent, in the stems to 38·0122 per cent, and in the roots to 28·5830 per cent. It is possible that the plant might be of value as a cheap "green manure" on account of its potash content. Compared with wormwood and fumitory wood, which, according to Hörs' analyses, afford respectively 9·74 and 21·9 per cent of ash, containing 74·94 and 36·48 per cent K_2O, the ash of the *Achyranthes aspera* is fairly rich in potash.

Medical College, Calcutta.

EXAMINATION OF MANURES, CATTLE-FOODS, AND SOILS.[†]

EXAMINATION OF ARTIFICIAL MANURES.

A.—*The Preparation of the Samples in the Laboratory, and General Determinations.*

1. DRY samples of phosphates or other artificial manures may be sifted and then mixed.

2. In moist manures, in which this cannot be effected, the preparation is confined to a careful intermixture.

3. On the arrival of the samples their weight is ascertained. One half of the sample is prepared for analysis,

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[*] Dymock, "Materia Medica of Western India."
[†] *Zeitschrift für Analytische Chemie.*

and the other, up to 1 kilo. in weight, is preserved in tightly-closed glass bottles in a cool place for a quarter of a year, reckoning from the day of despatching the report of the analysis, unless some other arrangement has been agreed on with the party sending the sample in question.

4. In crude phosphates and animal charcoal the moisture is determined at 105—110°, as a proof of identity. In samples which, during desiccation, may lose ammonia in any form whatever, this must also be determined.

5. Only average samples, carefully taken, and of at least 250—500 grms. and packed in well-fitting glass bottles, should be sent for analysis.

6. The weight of the samples sent in should be stated on the certificates of analysis.

7. In substances the moisture of which varies on pulverising the proportion of water must be determined both in the powdered and in the rough state, and the result of the analysis should be calculated according to the moisture of the original rough substance.

B.—*Examination of Phosphatic Manures.*

1. The extraction of superphosphates is effected by placing 20 grms. of the sample in a litre flask, pouring upon it 800 c.c. of water, and shaking it strongly and continually for half an hour, for which purpose a special machine has been invented, and may be set in action by hand or by any motor. About 150 rotations per minute are recommended. The flask is then filled up to the mark with water, the total liquid well shaken up and filtered. This process was introduced in the laboratories of the Association of Agricultural Experimental Stations on January 1st, 1891.

2. The solutions of double superphosphates must be boiled with nitric acid before the precipitation of the phosphoric acid, in order to convert any pyrophosphoric acid present into the tribasic acid. To 25 c.c. solution of superphosphate, 10 c.c. of concentrated nitric acid (1·4 specific gravity) are to be used.

3. In arbitration analyses the molybdenum method is to be used. The comparative determinations of superphosphate by the citrate method and the molybdenum methods as instigated by the commission must be made known at the next general assembly.

4. For determining the iron and alumina in crude phosphates the method of Glaser is for the present accepted as decisive :—5 grms. phosphate are dissolved in the known manner in 25 c.c. nitric acid of specific gravity 1·2, and in about 12·5 c.c. of hydrochloric acid of specific gravity 1·12, and made up to 500 c.c. 100 c.c. of filtrate, representing 1 grm. of the original substance, are placed in a ¼-litre flask, and 25 c.c. sulphuric acid of specific gravity 1·84 are added.

The flask is let stand for about 5 minutes and shaken for a few times, adding then 100 c.c. alcohol at 95 per cent, and cooling the flask, which is then filled up to the mark with alcohol and well shaken, when contraction takes place. The stopper is lifted, the flask again filled up to the mark with alcohol, and shaken again. After standing for half an hour it is filtered. 100 c.c. of the filtrate, representing 0·4 grm. of the original substance, are evaporated down in a platinum dish until the alcohol is expelled. The liquid, free from alcohol, is mixed with about 50 c.c. of water in a beaker and heated to boiling. Ammonia is then added until the reaction is alkaline, but not during the boiling, to avoid a violent effervescence. The excess of ammonia is driven off by boiling. The liquid is let cool, filtered, the precipitate washed with hot water, ignited, and weighed as ferric phosphate *plus* aluminium phosphate ; half the weight found is assumed as consisting of $Fe_2O_3 + Al_2O_3$. By this method the determination can be effected in from 1½—2 hours.

5. The fine meal in basic slag meals is determined according to the method agreed on at Bonn. The operation is as follows :—50 grms. ground slag are placed in a sieve with a surface of not less than 20 c.m. in diameter, and made of the wire tissue, No. 100, by Amandus Kahl,

of Hamburg (smooth texture), and shaken for fifteen minutes by hand or in a suitable machine.

6. For determining the moisture in superphosphates 10 grms. of the sample are heated to 100° for three hours; the loss of weight is assumed as water.

7. For determining phosphoric acid in bone-meal, fish guano, meat manure, and crude phosphates, as also total phosphoric acid in superphosphates, 5 grms. are dissolved in 50 c.c. aqua regia, consisting of 3 parts hydrochloric acid of specific gravity 1·12, and 1 part nitric acid of specific gravity 1·25, or it is boiled with 20 c.c. nitric acid of specific gravity 1·42 and 50 c.c. sulphuric acid of specific gravity 1·8 for half an hour.

C.—*Examination of Nitrogenous Manurial Substances.*

1. Nitrogen in the form of blood, flesh-meal, and similar organic matters, can be determined either by the Kjeldahl's process or with soda-lime.

2. Nitric nitrogen in mixtures may be determined according to Schlösing, Grandeau, or Lunge. Total nitrogen is determined according to the Kjeldahl-Jodlbauer or some similar process.

In Peruvian guano, whether crude or rendered soluble, the nitrogen, on account of the nitrates present must be determined by the Kjeldahl-Jodlbauer or by some analogous method.

3. For the determination of nitrogen in saltpetre a direct method should be sought for.

4. The total nitrogen in commercial ammonium salts should be determined by distillation with soda-lye.

Examination of Cattle-Foods.

The extraction of fats, which ought to be complete, is effected exclusively by means of ether free from alcohol and water. The weighed ethereal extract should dissolve in anhydrous ether without residue.

The commission is requested to explain the determination of fat in linseed cake by further experiments.

It was resolved to institute experiments concerning the degree of acidity of the extracted fat. It was recommended to use phenol-phthalein as indicator, and decinormal soda-lye as standard solution, as proposed by H. Fresenius, and to calculate the results as oleic acid—

$$\frac{C_{18}H_{34}O_2}{282}.$$
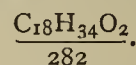
1 c.c. decinormal lye = 0·0282 grm. oleic acid. It was recommended to throw further light upon the value of the "iodine number" for the analysis of foods by its more frequent determination.

It was resolved to express the proportionate money-value of proteine, fat, carbohydrates, by 3 : 2 : 1.

(To be concluded).

ON THE DETERMINATION OF NITRATES IN WATER.*

By ALLEN HAZEN and HARRY W. CLARK.

(Concluded from p. 122).

II. *Aluminum Process.*

As usually described (Sutton's "Volumetric Analysis," Fifth Edition, p. 364), the aluminum process for the determination of nitrates consists of boiling a portion of the water with caustic soda, to expel ammonia, and after cooling, adding a piece of aluminum foil. The hydrogen evolved reduces the nitrates and nitrites present to ammonia. The hydrogen is taken through dilute acid to hold any ammonia that may be given off. After reduction is complete, the acid is washed into the water, and the ammonia distilled and nesslerised.

The process may be divided into two parts: the reduction to ammonia, and the estimation of the ammonia formed. For convenience we shall first consider the determination of the ammonia, and afterwards the conditions of complete reduction.

The amount of ammonia removed by the hydrogen is ordinarily so small that it seemed better to estimate its quantity and apply a correction, rather than use the troublesome absorption tubes of glass moistened with acid. The proportion of ammonia removed depends upon temperature and the amount of aluminum dissolved. Fifty c.c. of water saturated with ammonia at 20 degrees holds 26 grms. If the water contains 0·001 grm. of ammonia it is 1-26,000 saturated. One grm. of aluminum in dissolving gives off 1200 c.c. of hydrogen, and, supposing the ammonia to obey exactly the laws of gases, this should carry 1-26,000 of its volume of ammonia, or 0·046 c.c., weighing 0·000035 grm. or 3·5 per cent of the whole amount of ammonia present. With different amounts of aluminum, and the same volume of water, the loss is directly proportional to it, being 1·75 per cent when ½ grm. is dissolved. With different amounts of ammonia, the same percentage is removed. At higher temperatures the loss is greater, becoming 4·6 per cent at 30 degrees for 1 grm. of aluminum in 50 c.c. With reduced pressure the loss is greater, and is inversely proportional to the pressure. The loss from a nitrate solution is slightly less than from an ammonia solution, because there is no ammonia to be lost when the first hydrogen is given off.

Numerous experiments, keeping the acid separate from the bulk of the water, show that the above estimates are slightly above the truth, but they form a satisfactory basis for corrections, which practically never exceed 2 per cent.

We have found that, with ground waters at least, distillation of the ammonia after reduction is unnecessary, quite as good results being obtained by diluting an aliquot portion and nesslerising direct. The conditions of success of this process are that the water after reduction shall be practically colourless, and free from the black residue of the aluminum, and that no alumina shall precipitate before nesslerisation. The reducing action of the nascent hydrogen, with the caustic alkali and the carbonate always present, clarifies a majority of waters sufficiently, and it is only with the yellow swamp waters with low nitrates, where large volumes must be taken for the determination, that the colour interferes with the result. Waters usually settle so clear after the action that suspended matters are not troublesome. The separation of alumina causes the greatest difficulty, clouding the tube, and often seriously lowering the readings. This can be prevented by using for dilution distilled water entirely free from carbonic acid. Such water can be easily prepared by blowing steam through ordinary good distilled water. This treatment will also remove every trace of ammonia. Care

must also be taken that the carbonic acid of the breath does not come in contact with the water while measuring with a pipette.

When the aluminum-mercury couple suggested by Ormandy and Cowhen[*] is used, direct nesslerisation cannot be applied, for the separated alumina invariably holds a portion of the ammonia, and the results are too low. With caustic soda, however, at the end of the reaction, everything is in solution, excepting a slight residue of iron, &c., from the aluminum, and the portion nesslerised contains its full share of ammonia.

To determine how much aluminum must be dissolved to completely reduce the nitrates, the following experiments were made. The reductions were made in 50 c.c. Nessler tubes, on account of the convenience with which large numbers of tubes can be handled in racks, and the ease with which they are cleaned. (See Table below).

The amount of nitrite present at any point is comparatively small, and disappears promptly when the nitrate is all reduced, thus marking the end of the reaction. If we assume that the first centigrm. of aluminum in dissolving reduces 20 per cent of the nitrate, and each additional centigrm. 20 per cent of that remaining unreduced, we obtain the figures given in the last column. These agree fairly well with the observed reduction. The proportion of nitrate reduced by insufficient amounts of aluminum is almost exactly the same, whether the standard contains 1 or 10 parts nitrogen as nitrate in 100,000. With more dilute solutions, the proportion was nearly the same, but with stronger solutions the ratio is lower, although the absolute amount of nitrate reduced increases.

With higher temperatures, the solution of the aluminum is much more rapid and a smaller portion of the hydrogen is effective. At 30°, each centigrm. of aluminum in dissolving reduces only about 10 per cent of the unreduced nitrate, and so twice as much must be used to obtain a given reduction as is required at 20°. With temperatures lower than 20° the action is very slow, and a long time is required for enough aluminum to be dissolved.

If a large excess of caustic soda is used, the action is also very rapid, and the hydrogen is less effective, but the difference is not so marked as when the action is hurried by increased temperature.

The time required for the action depends upon the surface of the aluminum; the form of the metal has no other influence on the reduction. The same ultimate result is obtained with equal weights of aluminum, other conditions being the same, whatever its shape. With tin foil, the reaction is complete in a few hours, while with thick wire days may be required. When the tubes are allowed to stand over night at room temperature, foil 0·005 inch thick is thin enough, and gives less trouble by floating than thinner foil.

[*] *Jour. Chem. Soc.*, 1890, 811.

Potassium nitrate solution.		Aluminum. Grm.	Caustic soda. 40 per cent solution. C.c.	Nitrate unreduced. Per cent.	Nitrite. Per cent.	Nitrogen as ammonia. Per cent.	Calculated reduction. Per cent.
1 part N in 1000,000		0·01	1	82	2·5	15·5	20
		0·02	1	51·5	2·5	36	36
		0·04	1	35·5	2·5	62	59
		0·10	1	8	3·0	89	89
		0·20	1	0	0·5	99·5	99
		0·40	1	0	0·0	100	99·99
10 parts N		0·01	1	80	1·8	18	20
		0·02	1	63	3·0	24	36
		0·04	1	39·5	3·5	57	59
		0·10	1	15	2·0	83	89
		0·20	1	1	1·0	98	99
		0·40	1	0	0·0	100	99·99
0·1 part N		0·02	1	—	—	32	—
100 parts N		0·02	1	—	—	5	—

At one time we used a cheap caustic soda, containing zinc, because it was entirely free from nitrogen. It dissolved the aluminum freely, but for some unknown reason, the hydrogen evolved was less effective than that from other samples of caustic soda and potash. We thought this might be due to the zinc, but when zinc was added to pure caustic soda no corresponding effect was produced. The use of the soda was discontinued; but no explanation of its action has been found. The presence of sodium carbonate, even in large quantity, does not affect the reduction in any way.

With a majority of waters, the aluminum dissolves much more slowly than in distilled water, or in solutions of potassium nitrate in distilled water. Whatever the cause of this phenomenon, its effect is to make the hydrogen even more effective than with potassium nitrate solutions, as is shown by the following results with a ground water in which the aluminum dissolved very slowly:—

With 0·02 grm. Al. 0·45 part nitrogen reduced.
,, 0·10 ,, ,, 1·03 ,, ,,
,, 0·40 ,, ,, 1·03 ,, ,,

The proportion reduced by insufficient aluminum is considerably greater than with potassium nitrate solutions in which the aluminum dissolves more rapidly. Care must be taken in such cases that enough aluminum dissolves. Conditions which are best adapted to the reduction of potassium nitrate often fail completely with waters, because in the time which suffices for the complete reduction of the standard, the reduction of waters with slow action is far from complete. As with the phenolsulphonic acid process, the fact of good results with standards is insufficient evidence of good results with waters.

The absence of nitrites, as shown by the sulphanilic acid and naphthylamine test, is the best evidence that reduction is complete. As long as a decided red is given by these reagents, we may be sure that reduction is incomplete, but when only a slight reaction or no reaction is given, reduction is complete, and no higher results can be obtained by dissolving more aluminum. To obtain this result with waters, in a moderate length of time, it is necessary to use twice as much caustic soda as is required by potassium nitrate standards.

To make the determinations of nitrates in waters, we proceed as follows:—A 50 c.c. Nessler tube is filled to the mark with the water, and about 0·4 grm. aluminum foil 0·005 inch thick added with 2 c.c. of a 40 per cent solution of caustic soda. After standing eighteen to twenty-four hours at room temperature, a portion, 1 to 25 c.c., depending on the amount of nitrate present, is taken out with a pipette, and put in a tube of distilled water free from carbonic acid, which has previously been brought to the same temperature as the ammonia standards. All are nesslerised and compared in the usual way. Blanks and standards are frequently done as a control, and a portion of the waters, after reduction, is tested for nitrites. When nitrites are found in considerable quantity, the determinations are repeated, usually giving a higher result. In calculating the results, the correction for the volume of the caustic soda solution added, and the loss of ammonia with the hydrogen, and the reduction from ammonia to nitrogen, can all be combined in a single factor. When the determination is carried out as above, this factor is 0·88. Thus if 5 c.c. of the reduced water contains 0·05 m.grm. ammonia, 5 c.c. of the original water contained 0·88 of this, or 0·044 m.grm. nitrogen as nitrate. The blank should not exceed 0·005 part nitrogen in 100,000, and can often be neglected. Deduction is made for the ammonia and nitrites, but when the ammonia is a considerable fraction of the total nitrogen, it must be removed by boiling, after adding the caustic soda. In these cases, and also with waters having very low nitrates, especially yellow surface waters, the results obtained in this way are often unsatisfactory, both because the ammonia reading is influenced by the colour of the water, and because

the amount of ammonia obtained is too small for accurate estimation. In such cases, 100 c.c. or more of the water is boiled in a flask with the caustic soda to 50 c.c. The reduction is then made as usual, after which the ammonia is distilled in a current of steam and nesslerised. If the water is concentrated in an evaporating dish, the results are high, owing to absorption of nitrous acid from the gas, but in a flask, the blank is not more than 0·003 part, and is quite constant.

The following determinations of nitrates were made by one of us in solutions prepared by the other:—

Solution taken.	Nitrogen as nitrate taken. Parts in 100,000.	Nitrogen as nitrate found.	
Potassium nitrate..	0·20	0·21	⎫
,, ,, ...	1·52	1·48	
,, ,, ...	0·68	0·72	
,, ,, ...	1·76	1·67	Direct reading.
,, ,, ...	0·96	0·92	
,, ,, ...	1·46	1·50	
,, ,, ...	0·0	0·0	
,, ,, ...	1·20	1·20	
,, ,, ...	0·06	0·05	⎭
,, ,, ...	0 25	0·25	
,, ,, ...	0·010	0·009	⎫
,, ,, ...	0·044	0·043	
10 parts peptone	0·0	0·013	
10 parts peptone with potassium nitrate	0·027	0·046	
20 parts peptone	0·0	0·028	Distilled.
20 parts peptone with potassium nitrate	0·030	0·049	
10 parts egg albumen	0·0	0·020	
Sewage, albumenoid ammonia, 0·50	—	0·01	
Sewage, albumenoid ammonia, 0·72	—	0·02	⎭

With large amounts of organic matter, the action of the caustic soda and aluminum decomposes a portion of the organic matter with formation of ammonia, as is shown by the experiments with peptone and albumen. As far as our experiments have been carried, this error does not exceed from 2 to 4 per cent of the albumenoid ammonia. With almost all ground waters, and with most surface waters, this error is quite insignificant. It is only in presence of large quantities of decomposing organic matter that the result becomes uncertain. In such cases nitrates are invariably accompanied by nitrites, for if nitrate is added to such a water, a portion, if not the whole, is quickly reduced to nitrite, and in turn, the nitrite is often reduced, after all the nitrate is gone. We are thus able, in many cases, as for example with sewage, to infer the entire absence of nitrates from the low results, and the absence of nitrites. With excessive organic matter and the presence of nitrites, the results obtained can be taken as a maximum limit, and the same less 4 per cent of the albumenoid ammonia, as a probable minimum limit. It should be observed that the nitrate determination in such unusual cases is of minor importance, and that the phenolsulphonic acid process is also quite unreliable under these conditions, the organic matters giving a yellow colour which often corresponds to more nitrate than is shown by the aluminum process.

With potassium nitrate solutions in distilled water, the results are quite satisfactory, being as accurate as the strength of ammonia solutions can be determined at a single trial by direct nesslerisation, and we may believe that our results upon waters, with the above mentioned exceptions, are equally accurate.

Support in Weighing Substances.—H. Schweitzer (*Chemiker Zeitung*) recommends zylonite, a paper made from nitro-cellulose, camphor, and alcohol.

CORRESPONDENCE.

DETECTION OF NITRATES AND CHLORATES.

To the Editor of the Chemical News.

SIR,—The following two new tests for the detection of nitrates in the presence of chlorates, and of nitrates apart from chlorates, will, I opine, be found very simple and effective.

Nitrates in Presence of Chlorates.—Put together in a test-tube $KNO_3 + KClO_3 + H_2SO_4$ (dilute) + excess of Cu foil. Place test-tube in a beaker holding saturated solution of NaCl, and heat to boiling. The chlorate being least stable is first decomposed, the liberated chlorine attacking the Cu, and a greenish gas given off. At a higher temperature, KNO_3 is decomposed and attacks the Cu, with formation of *brown fumes*.

Nitrates Apart from Chlorates.—Put into a test-tube $KNO_3 + Pb$ foil (shavings) + HCl (strong) and heat ; KNO_3 is decomposed and attacks the Pb foil, with formation of $Pb(NO_3)_2$, which is again decomposed by the HCl, with formation of $PbCl_2$, and will be found as a white precipitate upon cooling.

One great advantage of this test lies in the fact that a nitrate can be detected in the presence of an iodide or bromide, because it is not dependent upon the formation of *brown fumes*, but upon that of $PbCl_2$. Thus—

$$Hg'_2(NO_3)_2 + NaBr + Pb\ foil + HCl =$$

free $Br + PbCl_2$ precipitate on cooling. Again,—

$$Hg''I_2 + KNO_3 + Pb\text{-}foil + HCl =$$
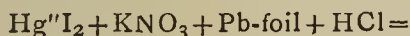
free $I + PbCl_2$ precipitate on cooling.—I am, &c.,

MATTHEW FORBES.

12, Bell Street, Dundee.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxiii., No. 8, August 24, 1891.

This issue does not contain any chemical matter.

Vol. cxiii., No. 10, September 7, 1891.

Direct Synthesis of the Primary Alcohols.— Paul Henry. — Methyl alcohol, H_3COH, is the primordial alcohol. The primary, secondary, or tertiary alcohols are derived from it by the respective substitution of hydrocarbon radicles C_nH_x for one, two, or three atoms of hydrogen. This general idea lacks experimental confirmation as far as the primary alcohols are concerned. The author has supplied this deficiency by the reaction of the organo-zinc compounds upon the simple monoclinic methylic ethers. These, $ClH_2C - OCH_3$ and $ClH_2C - OC_2H_3$, represent methylic alcohol, in which the hydroxyl group is rendered inactive in consequence of the replacement of the hydrogen by a hydrocarbon group, whilst the reactional aptitude of the chlorine is further heightened by the proximity of the oxygen. The monochloric methyl oxide, $ClH_2C - OCH_3$, and its ethylic analogue react energetically upon the organic zinc compounds. Into these, enclosed in a flask filled with carbon dioxide and strongly refrigerated, chloric ether is let fall drop by drop. There results a thick mass, a mixture of $ZnCl_2$ and of the ether formed. When the reaction is completed, water is added and the mixture is distilled. The yield of the operation is at least 90 per cent of the theoretical yield.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. vi., No. 67.

This issue is taken up with reports on the merits of the various inventors to whom the Society has awarded medals or prizes.

No. 68.

This issue contains no chemical matter.

Revue Universelle des Mines et de la Metallurgie. Series 3, June, 1891. Vol. xiv., No. 3.

Purification of Industrial Waters and Sewage.— A. and P. Buisine.—The authors prepare ferric sulphate from burnt pyrites by moistening them with concentrated sulphuric acid, so as to form a thick paste. If this is kept for some hours at 100—150°, with occasional agitation, the pyrites are covered with a whitish layer of ferric sulphate. It produces a more complete purification than does the addition of milk of lime. Water purified with ferric sulphate is perfectly clear, colourless, inodorous, neutral, or slightly acid. On the contrary, the effluent from the lime treatment is alkaline, coloured, retains an offensive odour, and rapidly becomes the seat of putrid fermentation. (Ferric salts have already been used for the treatment of sewage).

A New Method of Separating Iron from Cobalt and Nickel.—G. A. Le Roy.—In order to determine cobalt or nickel electrolytically, it is necessary first to remove any iron which may be present. The author effects this by bringing the metals into sulphuric solution, adding a very small quantity of a non-volatile organic acid, preferably citric. There is then added a large excess of a concentrated solution of ammonium sulphate, rendered strongly ammoniacal. Under these circumstances ferric hydroxide is not precipitated.

MISCELLANEOUS.

"**A Learned Judge! Mark, Jew, a Learned Judge.**"—A case was tried at the Belfast Assizes last week in which the plaintiff complained that his clothes had been destroyed and his flesh burned, by reason of the spilling of a corked bottle of aquafortis which had been served to him by the defendant. He had recovered £3 as damages, but was fool enough to appeal against that amount as being insufficient, the result of which was that he got nothing, and had to pay costs. To those who know anything about aquafortis, it may appear strange that any doubt could arise as to the stupidity of putting up that liquid in a corked bottle, but the evidence went to show that it is a custom of the trade to send it out in such way, and the learned judge was certainly not learned on this subject, for he said that he "never heard of aquafortis affecting corks before."—*Medical Press.*

Quantitative Determination of Pyridine Bases in Ammonia.—W. Kinzel (*Pharm. Central Halle*).—The author's method depends on the fact that pyridine and its alkyl derivatives, which in some respects are very similar to ammonia, form very unstable compounds with mercuric chloride, whilst ammonia forms more permanent basic compounds. The pyridine compounds are decomposed on heating and pass over into the distillate. 100 grms. of ammonia are neutralised with sulphuric acid (1 : 5) with thorough refrigeration (using tincture of litmus as indicator), mixed with 1 drop of soda-lye, made up to 400 c.c., and distilled down to 2/3 in an hour. The distillate is mixed with 10·0 mercuric chloride in solution again made up to 400 c.c., and again distilled down to 2/3 in the same time. The solution is again titrated with decinormal hydrochloric acid to a red colour, using dimethyl orange as indicator. As a small quantity of

ammonia always passes over into the distillate, corresponding under the above conditions to 0·8 c.c. of decinormal hydrochloric acid, this quantity must be deducted from the acid consumed. 1 c.c. decinormal acid corresponds to 0·0079 grm. pyridine.

On α-Naphthol-Benzeïn as Indicator.—R. Zaloziecki (*Chemiker Zeitung*).—The author obtains this compound in the following manner:—2 mols. α-naphthol and 1 mol. benzotrichloride are diluted in a flask with a suitable quantity of benzol, so as to reduce the violence of the reaction which commences at ordinary temperatures and to yield a much purer product. After standing for 24 hours the reaction is completed by heating to 30—40°, and benzol and the excess of benzotrichloride are driven off by a current of steam. The mass thus obtained is purified by dissolving in dilute soda-lye and fractionated precipitation with hydrochloric acid. This is repeated several times, and finally the colouring-matter is thoroughly washed, and appears as a red-brown powder. Traces of alkalies dissolve α-naphthol-benzeïn with an intense green colour, which is turned to a reddish-yellow by dilute acids. This reaction is occasioned also by carbonic acid, to which this indicator is extremely sensitive. Woollen tissue dyed green with this colouring-matter is turned orange on exposure to the air or on rinsing with spring water. α Naphthol-benzeïn dissolves in alcohol with a reddish-brown colour. A 1 per cent alcoholic solution is very well suited for volumetric purposes. In its entire behaviour α-naphthol-benzeïn completely resembles phenolphthalein, the only difference being with carbonic acid, since on the addition of an acid to a carbonate the change of colour takes place before the acid salt is formed.

TO CORRESPONDENTS.

J. P. C.—An account of the Kjeldahl process is to be found in Leffmann and Beam's " Examination of Water," p. 31 (Kegan Paul, Trench, Trübner, and Co., Lim.).

THE CHEMICAL NEWS.

VOL. LXIV., No. 1662.

ON DIDYMIUM FROM DIFFERENT SOURCES.*

By Professor C. M. THOMPSON.

IN the *Berichte* of date July 11th, 1887, Krüss and Nilson published observations on the rare earths producing absorption spectra, according to which almost every band observed was found to vary in strength in an independent manner, from which they drew the conclusion that the number of recognised elements must be very largely increased. These observations were continued by Kiesenwetter and Krüss, and the results previously obtained were confirmed.

The interest of these observations is chiefly in the fact that it is very difficult to fit such a number of elements into Mendeleeft's system of classification.

It appeared to me important that the purely experimental part of this work should be confirmed or corrected, and as I was in possession of several of the minerals from which the earths may be obtained, I have tried to repeat the observations.

I naturally selected for investigation those minerals from which the most striking results had been obtained, and in order to make my remarks more definite I will confine myself to the consideration of what may be called the didymium fraction. With respect to this fraction, perhaps the most striking results were those obtained by Kiesenwetter and Krüss with the minerals yttrotitanite and gadolinite.

According to them the solution of the earths from yttrotitanite showed only three bands due to didymium, two of them falling together in the broad band in the yellow; the other in the green. Now these are the strongest bands seen with an ordinary didymium solution, and they would of course be seen alone with a very weak solution. I found it impossible to use directly a very strong solution of the crude earths for the examination of the didymium fraction—the bands due to other fractions are so overpowering. The didymium was, therefore, precipitated in the usual way with potassium sulphate. On examining the solution of the nitrates of the earths thus precipitated, I saw, much to my disappointment, what I should describe simply as an ordinary didymium spectrum.

There remains the supposition that the mineral used by me was not the same as that used by Kiesenwetter and Krüss. I can only say that my mineral, like theirs, came from Arendal, and that it agrees in appearance with their published description. There are, however, two differences. The oxides of the earths got by me were of the usual fairly deep yellow colour; they describe their oxides as whitish grey with a tinge of yellow. Secondly, the number of bands not due to didymium, shown by a concentrated solution of my earths, is much greater than that mentioned by them, so that the whole spectrum is quite as complex as that shown by gadolinite earths.

According to Kiesenwetter and Krüss the earths from gadolinite from Hitterö show eight bands due to didymium. Separating the didymium fraction by potassium sulphate as before, I again obtained simply an ordinary spectrum. My gadolinite was from Hitterö.

I have further examined didymium from orthite and from monazite, and have been unable to observe any differences as compared with didymium from cerite which would justify me in concluding that the different bands varied in an independent manner.

I do not wish to deny that there may be slight differ-

ences, but they are certainly not such as I was led to expect from Krüss's papers, and they would require either quantitative measurements or direct comparison of the spectra to establish. I hope shortly to make a more careful comparison than I have as yet had time to undertake.

I am of course aware that no amount of negative results are of any value as against well-established positive ones, but I feel that some independent confirmation of Krüss's results is needed, and I can only hope that other chemists will be more fortunate in their material than I have been.

Notwithstanding the above remarks I am inclined to believe that the various bands which used to be ascribed to the one element didymium do vary in an independent manner.

As I pointed out in the CHEM. NEWS, vol. lv., p. 227, this conclusion follows from a combination of the results of Crookes and Auer von Welsbach. Only I have not found nature so kind in undertaking the labour of separation as Krüss appears to have done.

University College, Cardiff.

ON AN OPTICAL PROOF OF THE EXISTENCE OF SUSPENDED MATTER IN FLAMES.*

By Sir G. G. STOKES, Bart., F.R.S.
(IN A LETTER TO PROF. TAIT.)

8, Belgrave Crescent,
Edinburgh, June 13, 1891.

DEAR PROF. TAIT,—I write to put on paper an account of the observation I mentioned to you to-night, in case you should think it worth communicating to the Royal Society of Edinburgh.

In the course of last summer I was led, in connection with some questions about lighthouses, to pass a beam of sunlight, condensed by a lens, through the flame of a candle. I noticed that where the cone of rays cut the luminous envelope, there were two patches of light brighter than the general flame, which were evidently due to sunlight scattered by matter in the envelope which was in a state of suspension. The patches corresponded in area to the intersection of the double cone by the envelope, and their thickness was, I may say, insensibly small. Within the envelope, as well as outside, there was none of this scattering. The patches were made more conspicuous by viewing the whole through a cell with an ammoniacal solution of a salt of copper, or through a blue glass coloured by cobalt. In the former case the light from the flame was more weakened than the scattered light, which was richer in rays of high refrangibility; in the latter case the patches were distinguished by a difference of colour, the patches being blue, while the flame (with a suitable thickness of blue glass) was purplish. The light of the patches exhibited the polarisation of light scattered by fine particles—that is to say, when viewed in a direction perpendicular to the incident light, it was polarised in a plane passing through the beam and the line of sight.

When the beam was passed through the blue base of the flame there was no scattered light. A luminous gas flame showed the patches indicating scattered light like the flame of a candle, but less copiously. They were not seen in a Bunsen flame or in the flame of alcohol, but were well seen in the luminous flame of ether. When a glass jar was inverted over burning ether, the blue part, which does not show scattered light, extended higher till, just before the flame went out, the luminous part disappeared altogether. A Bunsen flame, fed with chloride of sodium, did not show the phenomenon, though the flame was fairly luminous.

The phenomenon shows very prettily the separation of carbon (associated, it may be, with some hydrogen) in the flame, and at the same time the extreme thinness of the layer which this forms. It shows, too, the mode of separation of the carbon, namely, that it is due to the action of heat on the volatile hydrocarbon or vapour of ether, as the case may be. At the base, where there is a plentiful supply of oxygen, the molecules are burned at once. Higher up the heated products of combustion have time to decompose the combustible vapour before it gets oxygen enough to burn it. In the ether just going out for want of fresh air, the previous decomposition does not take place, probably because the heat arising from the combustion is divided between a large quantity of inert gas (nitrogen and products of combustion) and the combustible vapour, so that the portion which goes to the latter is not sufficient to decompose it prior to combustion.

In the Bunsen flame fed with chloride of sodium, the absence of scattered light tallies with the testimony of the prism, that the sodium is in the state of vapour, though I would not insist on this proof, as it is possible that the test of scattering sunlight is not sufficiently delicate to show the presence of so small a quantity of matter in a solid or liquid state.—Yours sincerely,

G. G. STOKES.

P.S.—I fancy the thinness of the stratum of glowing carbon is due to its being attacked on both sides—on the outside by oxygen, on the inside by carbonic acid, which with the glowing carbon would form carbonic oxide.

PROF. LIPPMANN'S HELIOCHROMY.*

By F. E. IVES.

AT the March meeting of this Section I made some comments upon the alleged solution of the problem of photography in natural colours by Prof. Lippmann, of Paris, expressing some doubt as to the possibility of obtaining such alternate zones of "light and darkness" in proximity to the mercury mirror as are called for by Prof. Lippmann's theory, and also as to the possibility of reproducing the compound colours by means of interference lamina. I afterwards communicated my doubt to Prof. Himes, of Dickinson College, and asked for an expression of his opinion. He kindly wrote me a long letter, from which I quote as follows :—

"As far as I have been able to follow Prof. Lippmann I am more hopeful than you perhaps are in the direction of compound colours, and more nearly satisfied with the theoretical explanation, although, of course, at this early stage it must be regarded, of course, only as provisional, and there are many questions that both of us would like to ask, some of which Prof. Lippmann might possibly be able to answer by this time, and others I am just as certain he could not. I will just note hastily the points upon which I have less difficulty and doubt than you seem to have, premising first that you concede the fact that Prof. Lippmann has succeeded in getting a photographic impression of the spectrum in which can be recognised at least the colours in their order,—some say brilliant and perfect,—but I think Prof. Lippmann's account is more moderate and modest. But this is not the greatest feature of Prof. Lippmann's publication. This has been done long ago and by many, and possibly better than he has accomplished it, but he has succeeded in *fixing* it, and that by the ordinary photographic method, and his whole process, withal, is so simple and complete that it invites and encourages experiment with it, which I have great hope will lead to practical results.

"As to his theory we may think what we please. With me it has this in its favour, that the appearance of all previously obtained heliochromic results by Becquerel and others, whether flowing from systematic investigation or from accident, as in many cases, conforms to that of Prof. Lippmann's results, and can be best described as that of *interference* colours. There are even those who intimate that after all Prof. Lippmann adopted a theory and line of investigation already outlined.

"I have no difficulty in regard to the interference of direct and reflected waves so as to produce so-called stationary waves of definite length and frequency. The ocular demonstration of such waves, usually employed in lectures, by means of a stretched spiral cord or gum tube, attached at one end to a hook, and held at the other end by the hand, on which regularly timed impulses by the hand produce interfering direct and reflected waves, is very satisfactory at this point. The completed analogue in case of sound is to me conclusive of the plausibility of the theory of Prof. Lippmann. Savort, in the early part of the century, and more recently Lord Rayleigh (in 1888), by a series of classical experiments, demonstrated the presence of stationary sound waves, with their spaces of sound and silence, by the interference of direct waves with those reflected from a board, using a sensitive flame to explore the space. A double reflecting surface may be necessary to present interference colours to the eye, as you state, as the rays should both be moving toward the eye ; but to produce the stationary luminous undulations, or zones of maximum movement or maximum energy and zones of rest or of minimum movement, of the ether particles, the interference of an incident and reflected ray from one surface will be sufficient condition. These are hardly to be called zones of light and darkness. A ray of light is invisible as such ; it produces visible effects, so here the zones of differing energy in the ether particles produce varying effects upon the film in which they are formed—effects which we recognise as photographic.

"These effects are not the production of pigment colours, as up to this time seems to have been the expectation in heliochromy, but they are rather in nature of change of structure, laminated deposits of silver, so to say.

"As to the rendering of compound colours, I have not seen much claimed as accomplished in this direction. There is a well-grounded hope, I believe, but the rendering of the spectrum and the perfect fixing of it are the chief claims of Prof. Lippmann, as I understand it. I would not draw, or allow the theory to draw, the line of the impossible too near to the present achievement to prevent investigation and experiment with compound colours. The whole doctrine of perception of compound colours would not permit us to deny such possibility. Prof. Lippmann has certainly started scientific thought and investigation, as far as heliochromy is concerned, in a new direction, by results that command our admiration and a theory that is not only possible, but a most excellent working hypothesis."

Capt. Abney, who recently visited Prof. Lippmann, also appears to endorse his theories, but does not regard his process as a step in the direction of practical photography in colours. The following report of Captain Abney's remarks upon this subject, at the recent Camera Club Conference, is from the *Photographic News* of April 10th :—

"Photography in natural colours was the next question to which the President turned his hearers' attention. The 'accomplished fact,' as some of the newspapers led their readers to suppose, is as old as photography, for the discovery of photography in colours has been made, according to some people, over and over again. Being in Paris a week ago he had the opportunity of visiting M. Lippmann. He found that gentleman to be a true man of science, with all the modesty of a real investigator. The colour plates about which we have heard so much are due to interference, and not to pigments, and their effect varies according to the angle at which the plate on which they

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appear is held. Capt. Abney then proceeded to describe how these colours are obtained, by use of a mercury trough, as already detailed in our pages. He pointed out that, to obtain the colours, exposure to a bright spectrum was necessary, and that development must be brought about by alkaline carbonates, and the image intensified with silver. Both exposure and development must be exactly correct, or no colours are apparent, and the best results are gained with dry plates prepared with albumen and collodion. He looks upon the results of M. Lippmann's experiments merely as a verification of Newton's law, and not as a discovery of photography in colour. M. Lippmann has certainly succeeded in fixing interference colours, but the process is clearly one of extreme difficulty. It is a misfortune both for M. Lippmann and his predecessor, Dr. Koch, that their experiments should have been dealt with by the ordinary reporters, because these reports have led the general public to expect far more than the experiments in either case justified."

UNIVERSAL MICROSCOPIC EXHIBITION AT ANTWERP.

THE following particulars are obtained from the *Chemiker Zeitung* :—

The " Exposition de Microscopie Générale, de Produits Végétaux et d'Horticulture " has just come to an end. It was projected by Dr. Henri van Heurck, Director of the Antwerp Botanical Garden, a microscopist of reputation. The plan of the promoters allowed of a strange mixture of products. Thus, along with brewed drinks, " schnaps " of all kinds (*i.e.*, inferior liqueurs), were to be found pianos, mineral oils, guano and other manures.

J. D. Möller, of Wedel, in Holstein, exhibited a collection of Diatoms, including not fewer than 4026 distinct forms. Not alone photographs of these species were on view, but the original specimens could be examined under a number of microscopes.

The firm Lumière and Cöller, of Lyon, exhibited coloured transparent figures of microbia, just as they appear to the eye under the microscope.

Along with microscopes there were exhibited stoves for the cultivation of bacteria, apparatus for sterilising, &c.

Among the exhibitors of instruments a prominent place belongs to the establishment of Carl Zeiss, of Jena. Their display included a selection of microscopes, from the simplest to the most complex, combined with appliances for photographic projection, a set showing all the single parts of which a perfect microscope is composed, and a collection illustrating the production of lenses from the crude glass through every stage of grinding.

Watson and Sons, of Holborn, exhibited a large selection of microscopes for various purposes, especially an instrument made according to the indications of Dr. van Heurck, adapted for delicate researches and for photo-micrography.

M. Nachet, of Paris, displayed instruments for research, general, scientific, and technical.

Powell and Lealand, of London, exhibit a large microscope, said to be the most perfect as regards its stand. Hartnack, of Potsdam, had microscopes and object-glasses with photo-micrographic fittings. J. Deby, of London, displayed a collection of instruments by various modern makers with manifold appliances for illumination, arrangements for obtaining monochromatic light, as also a rich and interesting collection of preparations. Adnet, and also Wainsegg, of Paris, and Siebert, of Vienna, exhibited a variety of bacteriological apparatus.

It strikes us as remarkable that no spectroscopic apparatus seems to have been exhibited.

The *Chemiker Zeitung* remarks, with perfect justice, that it is impossible for an expert to pronounce on the value of any instrument so long as it can only be seen in a glass case.

ON THE
ACTION OF DIFFERENT METALS, METALLIC SALTS, ACIDS, AND OXIDISING AGENTS ON INDIA-RUBBER.*

By WILLIAM THOMSON, F.R.S.Ed., &c., and FREDERICK LEWIS.

A FEW years ago one of us studied the influence of different oily and greasy matters on india-rubber. (*Journal of the Society of Chemical Industry*, 29th December, 1885), and at the meeting of the British Association in Leeds we called attention to the distinctive effect which both metallic copper and all the salts of copper exercised on india-rubber. In the present paper we have carried these experiments further, with a view of obtaining more accurate information as to the effect of copper and its salts, and also that of other metals and their salts, and other agents, on india-rubber.

The method we adopted was to take a fine sheet of india-rubber spread on paper and vulcanised by the cold process with a mixture of chloride of sulphur dissolved in bisulphide of carbon. By this arrangement it was easy to tell the effect of different substances on the rubber on breaking the paper between the fingers, the fine sheet of caoutchouc being left free so that it could be stretched, and a fair idea obtained as to whether its elastic properties had been damaged.

Action of Metals on Rubber.

The first series of experiments was made with different metals reduced by means of a file to a fine state of division, the file employed being first thoroughly cleansed, and then washed with ether, to remove any oily or greasy matters from it. Small pieces of 3 inches square were cut from a large piece of the above-mentioned fine sheet pure Para rubber, and thin layers of the filings of the different metals were spread over about $1\frac{1}{2}$ inches square of the centre. These were then placed together in an incubator, kept constantly at a temperature of 140° F. by means of a thermostat, night and day, on glass shelves, and every day the positions of the pieces so treated were altered, so that those in the middle were placed nearer the sides, which we thought might possibly communicate more heat than might be received in the middle. After ten days the rubber on each square was tested in the manner above indicated. This series of experiments was repeated, and the following results were obtained :—

One of the metals had a destructive effect on rubber far beyond any of the others, and that was copper. As compared with copper the following metals had a comparatively slight effect, although they exercised an injurious influence. They are given in the order of the injurious influence they exercised :—

1. Platinum.	3. Aluminium.
2. Palladium.	4. Lead.

The following metals were tried, and found to have **no** effect whatever :—

Magnesium.	Tin.
Zinc.	Arsenic.
Cadmium.	Antimony.
Cobalt.	Bismuth.
Nickel.	Silver.
Iron.	Gold.
Chromium.	

Action of Metallic Salts on Rubber.

Saturated solutions of a number of metallic salts were made and painted over part of each small sheet of rubber (equivalent to about $1\frac{1}{2}$ inches square), allowed to dry,

and put into the incubator as above described. Along with each series several untreated small sheets of the same rubber were exposed for comparison, because, after some weeks, the pure rubber will itself become oxidised and lose its elasticity. Some insoluble or difficultly soluble compounds were also employed. These were mixed into thin pastes with water and painted on to the rubber sheets. The following substances entirely destroyed the rubber :—

Copper sulphate.	Silver nitrate.
,, chloride.	Strontium chlorate.
,, nitrate.	Vanadium chloride.
,, ferrocyanide.	Red oxide of manganese.
,, oxide.	Black ,, ,,
,, sulphide.	Bismuth chloride.
Arsenic iodide.	

The following substances *considerably damaged* the elasticity of the rubber, but did not entirely destroy it :—

Ferrous nitrate.	Uranium nitrate.
Sodium nitrite.	Ammonium vanadate.

The following substances only *slightly damaged* the elasticity of the rubber :—

Lead chromate.	Tin peroxide.
Ferrous sulphate.	,, perchloride.
Zinc acetate.	Chromic acid.
,, chloride.	Lead borate.

The following substances were found to have no action whatever on india-rubber :—

Ammonium sulphate.	Aluminium chlorate.
,, chloride.	Zinc chromate.
,, carbonate.	,, nitrate.
Potassium chromate.	,, oxide.
,, bichromate.	,, sulphate.
,, cyanide.	Ferric chloride.
,, acetate.	,, acetate.
,, carbonate.	Manganese chloride.
,, chlorate.	Cobalt chloride.
,, iodide.	Nickel chloride.
,, nitrate.	,, nitrate.
,, sulphate.	Thallium chloride.
Sodium sulphate.	Mercury bichloride.
,, sulphite.	,, iodide.
,, chloride.	Arsenious acid.
,, carbonate.	Arsenic acid.
Lithium carbonate.	Bismuth nitrate.
,, chloride.	,, oxide.
,, salicylate.	Cadmium bromide.
Rubidium chloride.	,, chloride.
Barium nitrate.	,, iodide.
,, chloride.	,, nitrate.
Magnesia.	,, sulphate.
Magnesium sulphate.	Lead chloride.
,, chloride.	,, oxalate.
Calcium carbonate.	Tin protochloride.
,, chloride.	,, protoxide.
Strontium chloride.	Palladium chloride.
,, acetate.	Gold chloride.
Aluminium sulphate.	

Effects of Minute Quantities of Copper Salts on India-rubber.

We next directed our attention to the influence of minute quantities of the salts of copper on india-rubber. We took small square sheets of the fine sheet rubber, adhering to paper, and painted one with a solution containing 10 per cent of sulphate of copper. On weighing the amount applied to the rubber it was found to be equivalent to 3·84 grains of crystallised sulphate of copper per square foot. This solution was then diluted with its own bulk of distilled water and a second sheet painted

with the diluted solution. This second solution was again diluted with its own bulk of water and a third sheet painted with it, and so on. There were thus prepared six pieces, containing the following quantities of copper salt per square foot of thin sheet rubber :—

	Grains of sulphate of copper ($CuSO_45H_2O$).	Equal to grains of copper oxide (CuO).
Sheet (a)	3·840	1·218
(b)	1·920	0·609
(c)	0·960	0·305
(d)	0·480	0·153
(e)	0·240	0·076
(f)	0·120	0·038
(g)	without copper.	

All these pieces were placed in the incubator at 140° F. for nine days, when it was found that the sample (f) which contained the smallest quantity of copper had entirely lost its elasticity and become quite rotten, whilst the piece (g) which contained no copper was perfectly sound; on examining the others they were all found to have entirely lost their elasticity, and to be hardened exactly in proportion to the quantity of copper salt placed upon their surfaces, (a) being the hardest. It is, therefore, evident that an extremely small quantity of a copper salt has a highly injurious influence on rubber with which it comes into intimate contact. In speaking on this subject to Mr. Thomas Rowley, of Manchester, he informed one of us that when he was an india-rubber manufacturer he had proofed large quantities of cloth with rubber, and had a book in which he kept samples of all he produced, many of which were now fifteen years old. It struck us that it would be interesting to find whether any of the cloths which had been so proofed, and which had remained good for so long, contained copper, and Mr. Rowley very kindly placed his pattern books at our disposal. These patterns were arranged in numbers, describing the nature of the cloth and kind of proof, &c., and dates. We selected seven samples, all of which, except one, had been steam vulcanised, *i.e.*, sulphur had been mixed with the rubber composition before proofing, and the combination between the two brought about by heating with steam afterwards. These patterns were perfectly sound, although about sixteen years old.

We also selected one pattern of a brown cloth, in which the rubber proofing was decomposed and hardened, and which broke on the cloth being folded or bent. Table A is the list of the samples taken.

All these samples were steam vulcanised, except the one marked 7th May, 1875, which was cold vulcanised with chloride of sulphur dissolved in bisulphide of carbon.

We carefully tested the whole of these for copper, and found that all those which were quite sound were perfectly free from it, whilst the sample which had become hard contained a trace of that metal. It appeared, therefore, that this trace was sufficient to bring about the complete destruction of the rubber after a number of years.

It may be well to give, as follow, the results of a series of experiments and analyses of some cloths, the rubber proofing on which was found to be destroyed within a few weeks or months after they were proofed. We pasted together, end to end, 19 samples of cloth, taken promiscuously, in one long line, and had the whole of them cut along the line into five equal parts. Each line of samples was then covered with a continuous sheet of different india-rubber mixtures, and one with pure Para rubber. Strips of each series were cut along the whole line, and then were looped and fixed so as to hang from stretched threads in the incubator, kept constantly at a temperature of 150° F. They were examined from time to time, but, finally, after twenty-five days, they were removed, and their condition noted; and, simultaneously, the analyses of unproofed pieces of the same cloths were made to find whether they contained copper, and the quantity of copper was esti-

TABLE A.

Private numbers.	Date	Description.	Results of analysis.	Condition in Jan., 1891
No. 110.	19 Nov., 1874.	Black alpaca.	Copper absent.	Good.
„ 222.	18 Jan., 1875.	„ „	„ „	„
„ 252.	22 Jan., 1875.	„ Paramatta.	„ „	„
„ 411.	2 April, 1875.	Blue-black Paramatta.	„ „	„
„ —	7 May, 1875.	Black fine sheeting (cold vulcanised).	„ „	„
„ 982.	28 Aug., 1875.	Brown fine sheeting.	„ „	„
„ 1150.	24 Sept., 1875.	Drab stout twill (black proofing).	„ „	„
„ 638.	25 June, 1875.	Brown cambric (black proofing).	Trace.	Quite decomposed and hard.

TABLE B.

	Per cent.		Appearance of rubber or rubber composition after being heated in the incubator at 150° F. for twenty-five days, in each of the five series.
Description of cloth.	Oily and greasy matters.	Copper CuO.	
1. White and black star check.. ..	0·260	Absent.	Good condition.
2. Dark brown ring check	0·384	Present, but copper not estimated.	Bad, and quite destroyed.
3. Light „ „	0·499	„ „ „ „	„ „ „
4. Dark brown check	0·128	Trace.	Damaged, but not quite hard.
5. „ broken check	0·516	Present.	Hard and quite destroyed.
6. Gold check	0·548	Absent.	Good.
7. Blue pin head check	0·648	Present.	Hard and quite destroyed.
8. Ruby hair line	0·301	Absent.	Good.
9. Drab fine sheeting..	0·264	„	„
10. Black and white small check sheeting	0·206	„	„
11. Black and white large check sheeting	0·445		„
12. Slate sheeting	0·181	,	„
13. Blue check sheeting	0·388	Trace.	Damaged, but not quite hard.
14. Crimson sheeting	0·471	Not tested.	Good.
15. Black fine twill	1·500	0·332	Very much damaged, rubber quite hard
16. Black broad	1·252	Present	„ „ „
17. Black sheeting	1·552	0·150	„ „ „
18. „ „	2·805	Present.	„ „ „
19. Black plain muslin	2·360	0·0157	Slightly damaged.

mated in some of them; the quantities of oily or greasy matters present were also estimated. Table B gives the results of the observations and analyses, and shows that the rubber remained good in all the samples of cloth which were free from copper, whilst it was more or less seriously damaged in all the samples which contained copper, and, still further, the damage sustained was, as nearly as could be observed, in direct proportion to the quantity of copper present.

The following pieces of cloth were analysed by one of us, because the rubber proofing had perished within a few weeks or months after being applied to them. Besides being analysed, a piece of each was taken, and one-third of it cut off and put aside. The oily and greasy matters were then removed from the other two-thirds by washing with ether; the part so washed was next divided into two equal parts, one put aside and the other boiled with 1 per cent hydrochloric acid solution, and washed till all the copper was removed and dried. These three pieces were then joined together, end to end, in a line, and attached to another black cloth similarly divided into three parts, one being left in its original condition, one having all the oily and greasy matters removed, and the third having both oily and greasy matters and copper removed; these were again joined in a line to a piece of grey cloth in its original condition, and to a piece of the same from which the oily and greasy matters were removed. It was, of course, unnecessary to use a third piece of this cloth, as it was free from any trace of copper. The eight pieces thus arranged in one line were divided along the line into two parts; one was covered with a continuous sheet of pure Para india-rubber, the other piece was covered with a rubber composition. Both were vulcanised by the cold process, and afterwards arranged in loops, and hung in an incubator at 140° F. for eight days. After that time

the rubber on both pieces of grey cloth and the two pieces of black cloth, from which both grease and copper had been removed (in both series), was found to be perfectly sound, whilst the rubber on the two black cloths in their original condition, and on the two from which the oily and greasy matters had been removed, but in which the copper remained, were completely destroyed, the effect of the oil and grease in contact with the copper. (Some of the copper contained in cloth is usually found in solution in the oily or greasy matters also present). The effect is to reduce the rubber to the condition of a soft sticky substance, resembling grease in consistency, and to this condition the proofing is soon brought when the oily matter present in copper-mordanted cloths exists in considerable quantity. The mixture thus produced is often absorbed into the fibre of the cloth, leaving it in a somewhat limp and sticky condition; when, however, the oily and greasy matters are removed, the rubber simply becomes hard. It is curious, therefore, to find that the

	Per cent.	
	Oily and Greasy Matter.	Copper Oxide (CuO).
Black Cloth ("I")	3·38	0·29
*Decomposed Proofed Cloth said to be same as above after proofing ("E") ..	—	0·12
Black Cloth ("M")	3·14	1·30
*Decomposed Proofed Cloth, said to be same as above after proofing ("C") ..	—	0·33

* These pieces were prepared by the same manufacturer, and said by the proofer to be from the same lots respectively as the unproofed cloths marked "I" and "M."

presence of copper, even when oily and greasy matters are absent, is almost as destructive to the rubber, on rubber proofed cloth, as when they are also present. The preceding table gives the proportions of oily and greasy matters present in the two samples of dyed cloth above-mentioned, and also the percentages of copper contained in them, and also the proportion of copper contained in two cloths, marked "E" and "C," which had been proofed, and become hard within a few weeks or months. Within the last few years a bright bluish black has been produced by means of copper salt with logwood, or more commonly by dyeing, first with logwood, using iron salts as a mordant, and finishing the dyeing with the use of a copper salt as a mordant; and it will be found that if cloth so dyed be proofed, the rubber will rapidly perish. It is remarkable that cloths proofed with a mixture of india-rubber containing a large quantity of "india-rubber substitute" (vulcanised oil) are not so easily affected by copper salts as those proofed with pure india-rubber. A curious piece of evidence as to the action of copper on rubber came into the hands of one of us, after proofing the above-mentioned pieces, which had been divided into three parts as above described, and obtaining the results just given. A chemist placed in our hands two pieces of the same black dyed cloth, which, he said, were produced by the same manufacturer, and proofed by two different proofers. He said he had heated part of them to 150° F. for a week, and they had not become injured in any way. Both pieces were analysed, and found to contain—

		Percentage of Copper Oxide.
India-rubber waterproofed cloth ..	(a)	0·190
" " " ..	(b)	0·108
Cloth before proofing	(c)	0·370
The oily and greasy matter in cloth before proofing amounted to ..		4·200 %

Wishing rapidly to arrive at a conclusion as to the influence of the copper oxide on the rubber, we heated pieces of both at the temperature of boiling water for twelve hours, along with two other pieces which were two and five years old respectively, and at the end of that time the rubber on the cloth containing copper was in the one damaged and in the other destroyed, whilst that on the two free from copper was quite sound.

We might give still another instance in which some black, brown, and white-check proofed cloth, the rubber on which had become oxidised and hard, was analysed by one of us, and found to contain 0·24 per cent of copper oxide: he afterwards obtained some unproofed cloth of the same kind, which he divided into three parts; one he left in its original condition, from one he extracted oily and greasy matters, and from the third he removed the copper as well as the oily and greasy matters; the three were joined together and covered with a continuous sheet of pure Para india-rubber by one proofer, and a second portion of these three pieces, joined end to end, was covered with a continuous sheet of ordinary rubber composition, containing lampblack, zinc oxide, and other mineral compounds, by another proofer. On heating these for fourteen days in the incubator, at a temperature of 150° F., the pure rubber and the rubber composition on the cloth from which the oily and greasy matters and copper were removed remained quite sound, whilst the proofed cloth, in its original condition, and in that from which the oily and greasy matters had been removed (leaving the copper), both the rubber and rubber composition had become quite hard.

The following gives the proportion of oily and greasy matters, and of copper contained in the unproofed cloth:—

	Per cent.	
	Oily and Greasy Matters.	Copper Oxide (CuO).
Unproofed black, brown, and white-check cloth	0·68	0·076

We think no stronger proof is necessary to show the enormous influence which a very small quantity of copper contained in cloth has upon india-rubber or rubber composition with which it may be covered or proofed.

We were under the impression that the action of copper on rubber had never been noticed by practical men employing rubber which requires sometimes to come into contact with copper. Speaking, however, to an electrical engineer and copper wire manufacturer who covers his wires with india-rubber, he informed one of us that the injurious action of copper on rubber was well recognised in his trade, and that to prevent this injurious action it was necessary to have the copper wire tinned, which was always done. We mentioned the matter to other electrical engineers, and found that all were quite cognisant of the injurious effects of copper wire on india-rubber. We found that copper filings also exert a highly injurious influence on thin sheets of gutta-percha when placed together in a warm place.

In looking at the effects of various chemical substances on india-rubber, it will be observed that the oxides of manganese have also a destructive effect on rubber, although not to such an extent as the copper salts; still it is important to india-rubber waterproof manufacturers, who are anxious to remove all possible causes of ultimate damage to their rubber or rubber composition covered cloths, to observe that the lamp black, ivory black, or other similar black, is free from the oxides of manganese, for one of us has found that in samples of such black compounds the heavy qualities sometimes contain a considerable proportion of these compounds.

The very curious nature of india-rubber is further shown by studying the tables of the actions of different chemical compounds on it. Some chemists have condemned cloths containing oxides of chromium for rubber proofing purposes, and they would regard the presence of even a trace of chromate or bichromate of potash as fatal, and the presence of free chromic acid in cloth would be regarded by them as an agent likely almost immediately to oxidise and destroy the rubber. Our experiments have shown that these bodies have little or no injurious effect on rubber, even when employed in large quantities and in concentrated solutions. It therefore leaves the logwood chrome blacks as available for use in the dyeing of cloths intended for rubber proofing. We observed a remarkable property of the iodide of arsenic, which we found might be used as a reagent to determine whether rubber sheet had been cold or steam vulcanised. When a solution of this substance is put upon india-rubber, vulcanised by the cold process, which consists in the application to the rubber of a mixture of chloride of sulphur and bisulphide of carbon, the chlorine from the chloride of sulphur, which remains in combination with the rubber, liberates the iodine from the iodide of arsenic solution, producing a dark stain, whilst no such effect is produced by unvulcanised india-rubber, or by rubber which has been steam vulcanised.

Action of Acids on India-rubber.

We have heard it asserted, from time to time, that a trace of sulphuric acid contained in india-rubber would soon determine its decay and decomposition. With a view to testing this point we took different acids, which were all brought to the same strength, viz., that 100 parts of the different acid solutions neutralised 100 parts of a 10 per cent solution of anhydrous sodium carbonate. These acids were placed in stoppered bottles, two bottles being half-filled with each acid solution, into each of which was immersed a thin sheet of rubber on paper as above described, about 2½ inches square; one of each was placed in the incubator and kept at 140° F. for a month, and the other kept during that time in the cold, the rubber in each being tested from time to time to ascertain whether the acids had any effect upon the sheets. The following acids were employed:—

Hydrochloric acid.
Sulphuric   ,,
Nitric   ,,
Chromic   ,,
Citric   ,,
Tartaric   ,,

In the first four the paper in the heated samples to which the fine sheet rubber was adhering was soon reduced to a pulp, leaving the sheet of rubber intact. After a few hours it was evident that the rubber in the nitric acid placed in the incubator had been seriously damaged, and after a few days it was so acted upon that its elasticity was destroyed, and after a month the whole of the rubber was reduced to a pulp, whilst at the end of the month the sheets of rubber in all the other acids remained as strong and elastic as they were on being first immersed. The sulphuric acid solution which had been heated in the incubator had darkened the colour of the rubber, but, so far as we could judge by stretching, it seemed to be stronger and more elastic than the original rubber. With a view to finding the effect of a minute quantity of sulphuric acid on india-rubber, we soaked a piece of thin sheet rubber in solutions containing 1-10th, 1, 2, and 5 per cent of sulphuric acid respectively, until the solution had thoroughly penetrated the sheet, which then appeared white. This was allowed to dry, and heated for some days to a temperature of 140° F., but the small quantity of acid exerted no injurious effect on the rubber. When, however, the rubber was taken from the strongest sulphuric acid solution containing 10 per cent of acid, dried and heated to 212° F. in a similar manner, it was soon destroyed. The sheets left in the cold for a month were likewise all sound except that placed in nitric acid, which was rendered quite friable, the elasticity having entirely gone.

Effects of Over Mastication on the life of India-rubber.

It has been so often asserted by india-rubber manufacturers that over mastication seriously damages india-rubber and leads to its rapid decay afterwards, that it seems extremely heterodox to say anything to the contrary. Still the results which we have obtained lead us to this opinion. In preparing rubber for spreading on cloth in the manufacture of waterproof fabrics, it it first passed between heavy rollers with a stream of waver pouring over it, to remove stones or dirt which might be associated with it; it is then dried thoroughly and masticated between large heavy smooth rollers for a few minutes, these being gradually screwed closer and closer together during the operation. This softens the rubber, and enables it afterwards to be brought into a uniform solution when mixed with the naphtha, and the longer it is masticated the less naphtha is afterwards required to bring it to the proper uniform consistency for spreading. It is highly improbable that over mastication would ever be done in practice, because the workman has to collect the rubber under the rollers and pass it repeatedly through them till it attains the necessary degree of softness, so that as it becomes over masticated it becomes soft and sticky, a point to which any experienced workman would not bring it. About four minutes is required for proper mastication, but one of us prepared some rubbers which were masticated for 15 and 21½ minutes respectively, and after spreading these on cloth we had a piece of the same cloth covered with properly masticated rubber (masticated during four minutes). All these were then placed in an incubator at 150° F. for a fortnight, but the sample of over masticated rubber did not show any sign of decay after that time, and to-day—six months after the experiment was made—the one appears quite as good as the other. The over masticated rubber had, when first produced, a slightly greater " tacky " feel than the properly masticated rubber, and this tackiness appeared not to have become greater or less after the lapse of six months.

Peroxide of Hydrogen.

The curious effect, or rather absence of effect, which chromic acid had upon india-rubber led us to make an experiment to find whether peroxide of hydrogen would oxidise and destroy it. We placed sheets of rubber both in alkaline and in acid solutions of that reagent for one month, and found that after that time the elasticity and strength of the sheets so treated remained unimpaired,—a result which appears quite as surprising as the chromic acid result. Some years ago one of us found that ozone exercised a most injurious influence on india-rubber, especially when it was left in a stretched condition, and it might naturally be expected that peroxide of hydrogen would have exercised an equally injurious influence on it.

CONTRIBUTIONS TO MICRO-CHEMICAL ANALYSIS.*

By H. BEHRENS.

XLVI.—*Phosphorus.*

1. MAGNESIUM salts are especially adapted for the detection of phosphorus in compounds which have been opened up by fusion with alkalies. Alongside a drop of the solution in question there is placed a second drop containing magnesium sulphate and ammonium chloride, the port. object is heated, and the two drops are made to coalesce by the addition of a drop of water, or of ammonia if no free alkali is present. Compare Magnesium 1. The limit of the reaction is at 0·000008 m.grm. P.

2. Ammonium molybdate is applicable in the examination of acid solutions in which ammonia would throw down insoluble phosphates. The precipitation ensues at the common temperature. It is accelerated by heat, but it must be remembered that arsenic molybdate and silico-molybdate may be deposited on the application of heat. Ammonium phospho-molybdate agrees with the analogous potassium salt. Compare Potassium 2. On thin slips of minerals containing apatite or phosphorite, a mixture of ammonium molybdate with rather strong nitric acid (1·3 specific gravity) applied in a thin layer and in the cold, gives a reaction which is very well localised. The limit of the reaction of ammonium molybdate with phosphoric acid has its limit at 0·000015 m.grm. P.

XLVII.—*Nitrogen.*

1. Nitrites can be recognised by means of potassium iodide and starch. Dilute sulphuric acid is applied, a few starch granules are suspended in the liquid, and lastly a little potassium iodide is introduced. Compare Iodine 5. Nitrates are reduced to nitrites by boiling with zinc or magnesium powder. More effective is fusion at dull redness on a nickel wire coated with lead. The limit of the reaction is at 0·00025 m.grm. HNO_3. If iron or manganese is present the conversion into ammonia is to be preferred.

2. Ammonia can be recognised without previous distillation as ammonium-magnesium phosphate. The solution in question is mixed with a *little* magnesium phosphate, and there is placed near it a drop of water in which sodium phosphate and bicarbonate have been dissolved. A gentle heat is applied and the two drops are caused to flow together. If calcium is present, magnesium chloride and soda-lye must be used, but it is difficult to avoid flocks of magnesium hydroxide. The limit of the reaction is about 0·00005 m.grm. NH_3.

Ammonia which has been isolated by heating with soda-lye, and receiving the vapour in sulphuric acid, is best recognised by means of platinum chloride in the same manner as potassium. Compare Potassium 1. The limit is here at 0·0001 m.grm. NH_3.

In order to detect nitrates in this manner the specimen is distilled with soda-lye and zinc-powder, and the same degree of sensitiveness is reached as in reduction to nitrites.

3. Most cyanides can be decomposed by caustic potassa. In this case it is sufficient to heat the strongly alkaline liquid with a small admixture of ferrous and ferric chloride, and then without much stirring to add dilute hydrochloric acid. As the iron hydroxide dissolves, flocks of Prussian blue appear. Mercuric cyanide requires to be reduced on bright iron with the addition of potassa-lye. The limit of the above reaction is at 0·00007 m.grm. CN.

XLVIII.—*Sulphur.*

1. Calcium salts give in neutral and acid solutions of sulphates a crystalline precipitate of $CaSO_4 + 2H_2O$. Compare Calcium 1. Sulphides must be prepared by fusion with saltpetre and soda, and insoluble sulphates by fusion with soda; the melt must be extracted with water, and the solution acidulated with acetic acid. The limit of the immediate reaction lies at the 400 fold dilution of the sodium sulphate. Beyond that limit the reaction may be masked by the presence of a large quantity of alkaline salts. As regards other disturbing influences, compare Calcium 1. Limit of the reaction 0·0002 m.grm. S.

2. Cæsium chloride, along with aluminium chloride, occasions in solutions of sulphates the formation of colourless octahedra of cæsium-alum. Compare Aluminium 1. This reaction is less simple than the former, but it is less readily masked by alkaline salts, and it is not interfered with by salts of iron. Its limit lies at 0·00012 m.grm. S.

3. Lead salts, on account of the minuteness of the crystals of lead sulphate, are used only for very dilute solutions of sulphates, or for such as are very strongly contaminated by other salts. The limit of immediate action is at a 40,000 fold dilution of sodium sulphate. Compare Lead 3. The limit of the reaction is at 0·000006 m.grm. S.

XLIX.—*Selenium.*

1. Magnesium, or in its place zinc, reduced slightly acidulated solutions of selenium dioxide. The selenium is deposited as a coating upon the magnesium. If, after a few minutes, the magnesium is dissolved by the addition of hydrochloric acid, there remain, if more than 0·05 per cent of selenium was present, complete impressions of the metallic fragments which are translucent with a deep red colour. From quantities of selenium below 0·02 per cent we obtain red flakes. The limit of this reaction is at 0·0001 m.grm. Se. The limit of the reduction by means of sulphur dioxide is at 0·02 m.grm. Se, according to Streng.

2. Potassium iodide throws down from solutions of selenium dioxide scarlet, pulverulent, selenium tetra-iodide. In solutions of seleniates the precipitation occurs only after heating with hydrochloric acid. Selenium iodide sublimes more readily than selenium; the sublimate does not differ in appearance from one of selenium. In an excess of potassium iodide there are formed orange or blood-red ribs and tables which may be mistaken for antimony iodide. By water they are decomposed, with liberation of amorphous iodide. The limit of the reaction is at 0·001 m.grm. Se.

(To be continued.)

The Phylloxera.—According to the *Chemiker Zeitung*, Prof. Perroncito, of Turin, has discovered a very efficient remedy for the Phylloxera. It is a liquid harmless to the vines and to the workmen, but rapidly fatal to the insect. Experiments made upon more than 200 vines in the Province of Porto Mauricio were very successful, whilst the expense of the treatment did not exceed 5 centimes per vine.

ON A COMBINATION OF WET AND DRY METHODS IN CHEMICAL ANALYSIS.*

PART I.

By W. E. ADENEY, F.I.C., Assoc.R.C.Sc.I., Curator, Royal University of Ireland; and T. A. SHEGOG, A.I.C., Assoc.R.C.Sc.I., Assist. Chemist, Royal College of Science, Dublin.

PLATTNER, in his work on the blowpipe,† states that, when the oxides of the metals are fused on charcoal with borax and sodium carbonate in the R.F., some are reducible and some non-reducible to the metallic state; and he has suggested a general scheme for the analysis of minerals based upon the possibility of separating the reducible from the non-reducible oxides when so treated. Plattner's scheme involves the employment of wet as well as dry methods of analysis. About 1 decigrm. of the substance is mixed with about 1 part of fused borax and 1 of sodium carbonate; the whole is wrapped in a little cylinder of soda-paper, and fused before the blowpipe in a hole on charcoal. As the quantity of reducible oxides is usually too small to obtain them in a single bead, about 1 decigrm. of metallic silver or gold should be added, in the form of a button, to take up the reduced metal as it is formed. In this way it is stated that a preliminary separation of the reducible from the non-reducible oxides may be effected. The reducible oxides are said to be those of the following metals:—arsenic, antimony, silver, mercury, copper, bismuth, thallium, lead, tin, zinc, indium, cadmium, and nickel. The volatile metals escape, either partially or wholly, during the fusion. The non-reducible oxides are those of the alkaline earths and of chromium, aluminium, iron, manganese, cobalt (in the absence of arsenic acid, and when not present in too large quantity), molybdenum, tungsten, and titanium.

The importance of Plattner's scheme, if it be generally applicable, cannot be exaggerated, for it permits the adoption of one general method of procedure for the qualitative analysis of all minerals, and avoids many of the difficulties attendant upon purely wet methods, such, for example, as the solution of substances, &c.; and, owing to its comparative simplicity, it is quite possible to teach the method to students in geology and engineering, who ordinarily cannot afford to devote sufficient time to master purely wet methods of mineral analysis.

Some time ago one of us framed a complete scheme for the analysis of minerals, based upon Plattner's methods. The substance was to be fused with silver chloride, borax, and sodium carbonate on charcoal in the manner described by Plattner. In cooling the metallic end glass beads were to be carefully detached, one from the other, and separately examined by wet methods in the ordinary way.

Complex minerals, such as tin pyrites and smaltine, were analysed, as directed in this scheme by Mr. F. C. Forth—a student in the Faculty of Engineering in the Royal College of Science, with excellent results. The following are the results of his analysis of smaltine:— arsenic, bismuth, copper, nickel, cobalt, iron, aluminium, manganese, calcium, magnesium, sodium, siliceous matter, hydrosulphuric acid, and phosphoric acid.

On comparing these results with those of an analysis by the ordinary wet methods, it was found that potassium only had escaped detection.

When, however, the method was tried with iron and zinc ores, unsatisfactory results were obtained—results which were in some cases not what we had been led to expect from a perusal of Plattner's book—for instance, with the ores mentioned, the glass bead fused fairly easily, but the metallic bead immediately on reduction became quite infusible, and could not be properly separated from the glass.

Plattner, in describing his process and the results obtainable by it, makes no mention of such action. Egleston, too, in his scheme makes no reference to it.*

On examining Plattner's work carefully, it was seen that no exact experimental evidence was given by him in support of his classification of the metals into "reducible" and "non-reducible," according to their behaviour on fusion with borax and sodium carbonate on charcoal, in the reducing flame.

It became evident to us from these and other preliminary experiments, that Plattner's method was not one by which easily reducible oxides and difficultly reducible oxides could under all conditions be completely separated. The same may be said of Egleston's method.

The results, however, obtained by Mr. Forth in the analysis of smaltine and tin pyrites were, as above stated, so satisfactory as to convince us of the value of the method if carefully worked out. We therefore determined to make an exhaustive series of experiments, in order to ascertain exactly how the various metals behave when their compounds are fused with borax and sodium carbonate on charcoal in the reducing flame in presence of silver.

We were further encouraged to make these experiments by some quantitative estimations of the nickel, cobalt, bismuth, and copper in the smaltine, made by Dr. L. Davoren, who was at that time studying in the laboratory of the Royal College of Science. Dr. Davoren determined these constituents both by the ordinary wet method and by the proposed combination of wet and dry processes. His results were as follows :—

	Ordinary Wet Method. Per Cent.		Wet and Dry Processes. Per Cent.
Nickel	7·60		7·31
Cobalt	3·73		3·92
Bismuth. ..	2·32	I.	3·33
		II.	3·35
		III.	3·33
Copper	1·80		2·06

These results led us to hope that the method might (possibly with some modifications) be found capable of employment for quantitative as well as for qualitative analysis.

The questions we wished to settle by our experiments were :—

1. Whether, when fused in the reducing flame on charcoal with borax and sodium carbonate, the metals antimony, tin, lead, arsenic, silver, bismuth, copper, nickel, and zinc could be completely reduced from their combinations with oxygen with the volatile acids, hydrochloric, sulphuric, nitric, and hydrofluoric ; and also from their combinations with the non-volatile acids, silicic and phosphoric.

2. Whether, when similarly treated, aluminium, chromium, manganese, cobalt, and iron are wholly non-reducible from their compounds ; the cobalt and iron more especially from their combinations with arsenic and phosphoric acids.

3. Whether, when *complex* substances are similarly treated, the constituent metals thereof respectively behave as in simple compounds, or whether their behaviour is modified in any way.

The subject-matter of the present paper deals mainly with questions Nos. 1 and 2. A considerable amount of work has also been done bearing upon question No. 3, but it is proposed to deal with this, and with separations by this method, in a further paper by one of us.

Tables are appended giving the results of some of our experiments

(To be continued).

NOTICES OF BOOKS.

Engineering Chemistry : a Practical Treatise for the Use of Analytical Chemists, Engineers, Iron Masters, Iron-Founders, Students, and others. Comprising Methods of Analysis and Valuation of the Principal Materials used in Engineering Work, with numerous Analyses, Examples, and Suggestions. By H. Joshua Phillips, F.I.C., F.C.S., Analytical and Consulting Chemist to the Great Eastern Railway, Author of "Fuels, Solid, Liquid, and Gaseous : their Analysis and Valuation." London : Crosby Lockwood and Son. Crown 8vo., pp. 312.

THE chemical properties of many articles used in what is somewhat loosely called "engineering work" are necessary data for determining their value. Hence we need not prove that the author in collecting together a series of well-proved methods for the analysis of such materials has rendered no small service to a numerous body of practical men.

The introductory chapter of the work is occupied with an account of the Reddrop "equivalent system" of reagents—a full account of which will be found in the CHEMICAL NEWS (vol. lxi., pp. 245, 256).

In Part I. Mr. Phillips proceeds to the analysis of metals and alloys, including white-lead. Next follow ores, limestones, boiler incrustations, clays, blast-furnace slags, &c. In Part III. the author embodies the substance of his former valuable work "Fuels, Solid, Liquid, and Gaseous" (Crosby Lockwood and Son, London). Part IV. is concerned with water. All that is said concerning water for steam-purposes, and the determination of its possible mineral constituents, is perfectly to the purpose, and will be found trustworthy.

In a number of analyses of American samples we regret to find that "the constituents have been stated in grains per U.S. gallon of 231 cubic inches, rather than in parts per 100,000, the former being in general use by the mechanical profession as the proper method by which to express the weights of the component parts of water." This method seems to us devoid of any advantage. Chemists, medical men, &c., in Britain state the contents of water (other than H_2O), either in grains per imperial gallon (=70,000 grains) or in grains per 100,000, or in parts per million, or again, as do our Continental colleagues, in grms. per litre. The introduction of an additional scale can merely tend to confusion.

The injurious effects of magnesium chloride in steam waters are clearly pointed out. The examination of water for drinking purposes can scarcely be said to belong to engineering chemistry. For the determination of free and albumenoid ammonia the author uses the well known Wanklyn process. Concerning the microscopic and biological methods for the examination of drinking waters, the author merely remarks that "many of the diseases that human flesh is heir to are propagated through the drinking of water contaminated with microscopic creatures."

We are little edified at finding here a reproduction of the "standards" of the Rivers' Pollution Commissioners. The errors in principle and the inconsistencies in detail of these "recommendations" have been so often and so ably exposed that charity to their authors, no less than to the public, demands their consignment to oblivion.

The section on oils, lubricants, illuminants, and on materials serving for promiscuous purposes, is admirably written and will be found very useful.

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* Egleston, in his scheme, confines himself almost exclusively to dry methods. His method of preparing the glass bead is different to that employed by Plattner. He dissolves the substance in a borax bead on platinum wire, and, when saturated, tosses it off into a porcelain dish, and repeats this operation until a number of beads have been obtained. He then treats the beads on charcoal with lead, silver, or gold in the reducing flame; separates the metallic from the glass bead, and examines each separately by dry methods. The only use he makes of the wet way is in the examination of the borax bead for chromium, titanium, molybdenum, niobium, tungsten, and vanadium. The metals which, according to him, may be present in the metallic bead, are nickel, copper, silver, gold, tin, lead, and bismuth (tin, lead, and bismuth being partially volatilised).

In the four remaining parts the author discusses the materials used in grease-making, gas-works products, disinfectants—which seem somewhat out of place—and explosives.

An appendix of useful tables completes the work.

The analytical methods may be pronounced most satisfactory, being as accurate in their character as the dispatch required of engineering or, indeed, of all industrial chemists permits.

The only alterations we can suggest is a re-calculation of the analyses of boiler-waters—pp. 164 and 165—either to the imperial gallon or to 100,000 parts.

The Metallurgy of Silver. A Practical Treatise on the Amalgamation, Roasting, and Lixiviation of Silver Ores, including the Assaying, Melting, and Refining of Silver Bullion. By M. EISSLER. Second Edition, Enlarged, with 150 Illustrations. London: Crosby Lockwood and Son. Crown 8vo., pp. 362.

THE metallurgical writings of M. Eissler are so highly appreciated by competent judges that we are by no means surprised that a second edition of the work before us has become necessary.

Upon the whole the present edition differs so little from its predecessor that what we have already said at its appearance requires no modification. A defect, or rather an inconvenience, for the English reader is that the yields of different ores by the processes described are expressed neither in percentages nor in the weights of precious metal per ton, but in its value as expressed in American money.

The supplementary chapter gives an account of the Boss "one level system and amalgamating pan," of Brunton's ore sampler, of roasting with salt, with the question what furnace to adopt, of the Bowers and the Thompson furnaces, and a very interesting notice of the behaviour of other metals in the amalgamation of silver ores.

M. Eissler does not think that silver ores carrying even a considerable proportion of oxidised copper yield a cupriferous bullion in the Washoe process. The presence of copper amalgam in the mercury is very beneficial in silver extraction. Lead is not a desirable substance in amalgamation. Zinc is usually expelled by roasting prior to amalgamation.

Iron, it appears, is capable of amalgamating with mercury, but under what conditions it is still doubtful. It is "one of the prime motors in furthering the amalgamation of silver." Antimony is generally expelled by roasting, as is also arsenic, which is a " bad metal to get into the pans,"—a very true remark.

Manganese, in roasted ores, is apt to form a thick froth which holds fine particles of mercury in suspension.

article on the skins of infants ; or in other cases the certificates may state that a certain food for infants contains everything that is requisite for the healthful nutrition of children, whereas *bona fide* analyses may show that it is deficient or wanting in some of the ingredients essential to infantile alimentation, and the experience of its sole use as a food may be that it is the causative factor of rickets, or of the scorbutic condition, in children.

The sale of such certificates is, in my opinion, degrading to the profession of chemistry, immoral on the part of those from whom they emanate, and misleading to the public ; and those who sell such certificates for money are unworthy of the title of professional men. This prostitution of the science of analytical chemistry must be checked if analysts wish their profession to take its place in the estimation of the public as a calling worthy of the name of a learned profession.

Bearing in mind the fact that each Fellow of the Institute of Chemistry signs a declaration to the effect that he will demean himself honourably in the practice of his profession, and to the utmost of his power maintain the dignity and welfare of the Institute, I have for some time been wondering if the Censors of the Institute of Chemistry are an existing body, and, if so, why signs of their existence are not evident to us. Surely part of their duties must be to exercise a controlling power over the professional actions of those Fellows of the Institute who have the bad taste to allow their names to be flaunted before the public in connection with certificates of a puffing description ; certificates which too frequently bear the impress, not of the results of analysis, but of statements which, to put it mildly, are frequently exaggerated, and, to put it less mildly, are frequently untruthful.

I am fully aware that many will retort that these things are done by some members of the medical profession. While admitting that such, unfortunately, is the case, yet two wrongs do not make a right, and certainly such things are not done at the present time by members of the higher ranks of the medical profession. As regards the section of the medical profession to which I belong, viz., physicians, the College of Physicians of London exercises, through its Board of Censors, a strict supervision over the Fellows and Members of the College, and, in my opinion, it would be well if a similar strict supervision were exercised by the Censors of the Institute of Chemistry over the Fellows and Associates of the Institute.

As a Fellow of the Institute of Chemistry I sincerely hope that it will soon rise from the level of a mere examining body to that of a body exercising a just, but vigilant, supervision over the actions of its Fellows.—I am, &c.,

ARTHUR P. LUFF, M.D., B.Sc. (Lond.), F.I.C.

47, Weymouth Street, W., Sept. 25, 1891.

CORRESPONDENCE.

THE INSTITUTE OF CHEMISTRY AND ADVERTISING CERTIFICATES.

To the Editor of the Chemical News.

SIR, — For some time past it has been no uncommon occurrence to those who read the advertising columns of the daily papers, journals, &c., to see advertised copies of certificates of analyses, or certificates without any analysis appended, given by analytical chemists after whose names the letters F.I.C. appear. In some cases these certificates may state that a certain article is incapable of injuriously affecting an infant's tender skin, whereas the experience of physicians may be that it is by no means an uncommon occurrence for eczema, or some other skin disease, to result from the use of such an

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed

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Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxiii., No. 11, September 14, 1891.

On the Ferment of Wine.—A. Rommier.—The author adduces further experimental evidence that the bouquet of a wine depends on the ferment employed, and that by utilising this fact ordinary vineyards may be made to produce wines equal to the *"grands crus"* of Burgundy. (The question arises whether the ferments of the choicest French, Rhenish, and Hungarian wines may not be communicated to the growths of South Africa and Australia ?)

Zeitschrift fur Analytische Chemie.
Vol. xxx., Part 2.

Contributions to Micro-Chemical Analysis.— H. Behrens.—(Already inserted).

Conversion of Free Nitric Acid into Ammonia by Nascent Hydrogen.—Dr. Karl Allsch.—This paper requires the accompanying illustrations.

Liquoscope : an Instrument for the Optical Comparison of Transparent Liquids.—Klas Sonden.—This paper cannot be intelligibly reproduced without the four accompanying illustrations.

Densimetric Determination of Phosphorus in Crude Iron.—E. E. Metz.—This memoir also requires an illustration.

Glaser's Method of Determining Ferric Oxide and Alumina in Phosphates.—Dr. von Gruber. —The author defends Glaser's method against the strictures of Dr. Theodor Meyer.

The Aldehyd Reaction of U. Gayon.— H. Borntrager.—Already inserted.

Improved Apparatus for the Determination of Carbonic Acid.— Greiner and Friedrichs.—This paper depends on the accompanying diagram.

Use of Mohr-Westphal's Balance.—A. Gawalowski. —The author points out as a difficulty in the use of the Westphal balance, that the fine platinum wire by which the thermometer-float is suspended easily becomes bent and is difficult to straighten. This can be easily effected by stretching it horizontally whilst being passed through the flame of an ordinary spirit lamp.

Determination of Manganese in Iron and Steel.— L. Blum.—Already inserted.

The Visible and Ultra-Violet Emission-Spectrum of Burning Faintly Luminous Hydrocarbons.—J. M. Eder.—No particulars are given, the reader being referred to the *Denkschriften de Mathematisch Naturwissenschaft. Classe de K. Akademie der Wissen in Wien*, vol. lvii.

A Spectro-Saccharimeter.—P. Glan.—This instrument, which is described at great length, is intended for accurate determinations of the deviation of the plane of polarisation of light, and for rendering such measurement practicable for every colour of the spectrum.

A Crystal Refractometer.—S. Czapski.—The principle of this instrument is the same as that of Pulfrich.

The Application of Lunge's Gas Volumeter to the Determination of Tensions.—Herm. Rey.—Not adapted for abstraction, requiring the appended tables.

Determination of the Specific Gravity of Rare and Costly Substances.—Aug. Eichhorn.—The instrument has the form of a hydrometer. Between the mercury bulb and the empty float a hollow globe is blown on the stem containing the liquid to be weighed. The stopper is inserted in such a manner that no air globules remain within, and the whole is set in a vessel filled with water at 15° or 17·5°. A scale fixed to the instrument gives the direct specific gravity.

A Table of Corrections for the Gas-Balance of Lux.—R. Mehmke.—The table is not given here.

Thermometers and Measurements of Temperature.—H. F. Wiebe.—Mercurial thermometers filled with nitrogen may be used for the determination of temperatures even exceeding 450°, if they have been previously protected by prolonged heating, and if they are so constructed that the pressure exerted by the nitrogen upon the mercury at 450° is about 4·5 atmospheres.

Thermostats and Thermo-regulators.—O. Foerster. —Not adapted for abstraction.

Air-Bath.—A. Adams.—From the *Analyst.*

A Small Trial Filter.— P. Boessneck (*Chemiker Zeitung*).—A simplification of the tube filter described in "Mohr's Manual of the Volumetric Method."

Apparatus for Distilling Mercury in Vacuo.— Dunstan and Dymond.—From the CHEMICAL NEWS.

Support for Filtering Several Precipitates at Once.—E. Sauer (*Chemiker Zeitung*).—This instrument is intended for cases where the filtrates do not require to be preserved.

Separation of Small Quantities of Supernatant Liquids.—E. Drossaert (*Chemiker Zeitung*).—A small syphon drawn out and turned upwards like a hook at the end of the shorter limb.

Permeability of Caoutchouc Tubing for Carbonic Acid.—F. Kolbe.—A tube 77 c.m. in length and 8 m.m. in width, with sides 2 m.m. in thickness, allowed 6 c.c. of carbonic acid to escape hourly.

Application of Hydrogen Peroxide for Determining the Value of Chloride of Lime, Pyrolusite, and Permanganate.—G. Lunge (*Zeit. Angew. Chemie*).— This paper will be inserted at some length.

Standard in Acidimetry and Alkalimetry.— H. Heidenhain (*Chemiker Zeitung*).—The author recommends as standard potassium bitartrate.

Agent for Opening up Minerals.—C. A. Burghardt. —From the CHEMICAL NEWS.

Preservation of Sulphuretted Hydrogen Water.— Firemi (*Chemiker Zeitung*).—The author has bottles with glass capsules fused to the neck round the stopper. The capsule contains a layer of a mixture of glycerin and water 4 to 5 m.m. in depth, whilst a small glass bell covering the stopper dips into the capsule.

Separation and Determination of Nickel and Cobalt.—Constantine Kraus (*Mittheilungen aus dem Laboratorium der Universität Erlangen*).—A critique of the known methods which will be inserted successively.

Determination of Manganese in Iron and Steel.— L. Rürup. - Already noticed.

Determination of Camphor in Celluloid. — F. Foerster.—The object is decomposed by treatment with soda-lye, the camphor is driven off by distillation, separated from the distillate by means of measured quantities of benzol, in which the proportion of camphor is determined optically.

Determination of Value of Solutions of Mercuric Chloride, &c.—J. Bongartz.—The chlorine of an aqueous solution is determined volumetrically.

Optical Valuation of Quinine and Cinchonidine. —O. Hesse.—The author questions the applicability of the optical methods of De Vrij, Oudemans, and Kopposchaar.

Determination of Alkaloids in Narcotic Extracts. —O. Schweissinger and G. Sarnow.—The authors dissolve 2 grms. extract in 8 c.c. water, add 2 c.c. ammonia, and shake up with a mixture of 15 parts chloroform and 25 parts ether.

Reaction of Morphine with Sulphuric Acid and Phosphates.—Vulpius.—If a few drops of a liquid containing at least $\frac{1}{4}$ m.grm. of a morphine salt is mixed with six drops undiluted sulphuric acid, a few c.grms. of sodium phosphate are added, and the capsule is heated over a flame with constant stirring, there appears a violet colour. On adding to the cold mixture water, drop by drop, it turns bright red, and finally a dirty green.

Examination of Manures, Cattle-Foods, and Soils. —Procedures adopted at the third general meeting of the Union of Agricultural Experimental Stations. The methods for sampling and analysis will be given in detail.

Determination of Mercury in Animal Tissues.— E. Ludwig and E. Zillner comminute the parts and boil them over an open fire with an equal weight of hydrochloric acid at 20° in a flask fitted with a Liebig's condenser until all the solids are dissolved. When the liquid

has cooled down to 60° a few grms. potassium chlorate are added in portions of ½ grm. The cold liquid is filtered, the filter rinsed, and the entire liquid is repeatedly mixed with a few grms. of zinc-powder, whilst constantly stirring. From the dried mass the mercury is separated by a process of distillation.

Determination of Urea.—S. H. Smith.—(From the *Pharm. Journal*). Short notices follow on the detection of sugar in urine and in blood; of phenols in urine and of melanine in urine.

Distinction between Arsenical and Antimonial Spots obtained by the Process of Marsh.—G. Denigés.—From the *Comptes Rendus*.

The Colour Reactions of Strychnine. — C. L. Bloxam.—(From the CHEMICAL NEWS). For certain methods for the detection of strophantine and cocaine we refer to the original.

MISCELLANEOUS.

Examination of Glass.—F. Mylius (*Berichte Deutsch. Chem. Gesel.*).—The objects to be examined are carefully washed with water, next with alcohol, and then with ether, and whilst still moist with ether they are treated with a solution of eosine. To prepare this solution commercial ether is saturated with water by agitation, and o·1 grm. of iodeosine is dissolved in every 100 c.c. The decomposability of the glass may be judged by the colouration produced.

Handbook of Industrial Organic Chemistry.— A work under this title by Prof. Samuel P. Sadtler is about to be issued by Messrs. Lippincott and Co. It will be a work of value to those interested in the application of Chemistry to the arts and manufactures, and will bring together within the compass of a moderate sized volume a mass of information with regard to materials, processes, and products of most important industries, such as could not be obtained except by prolonged search through a large number of special works and technical journals. At the same time, the bibliographical lists attached to each chapter will make it possible for the authorities to be rapidly gathered in any particular case. The work will be published in a large octavo volume of 519 pages, and will be illustrated by cuts of the most approved apparatus employed in the various industries.

THE CHEMICAL NEWS.

VOL. LXIV., No. 1663.

ON THE REACTION OF GLYCERIDES WITH ALCOHOLIC ALKALIES.*

By ALFRED H. ALLEN.

THE natural fats and fatty oils are commonly regarded as consisting, with a few exceptions (*e. g.*, sperm oil), of the glycerides of the fatty acids. It rarely, if ever, happens that a natural fat consists merely of a single glyceride, and there is good reason to believe that in many cases different fatty acid radicals occur in the same molecule. Butter-fat is a good illustration of this, for the butyrin cannot be separated by any process of fractional solution from the less soluble glycerides. On saponification it yields butyric acid, and acids which are generally considered as being oleic and palmitic acid;† besides smaller amounts of arachidic, stearic, myristic, and lower acids of the stearic series. The result of saponifying a complex glyceride molecule containing the radicals of butyric, palmitic, and oleic acids, is shown by the following equation :—

$$C_3H_5 \begin{cases} O.C_4H_7O \\ O.C_{16}H_{31}O \\ O.C_{18}H_{33}O \end{cases} + 3K.OH = C_3H_5 \begin{cases} OH \\ OH \\ OH \end{cases} + K.O.C_4H_7O +$$
Glycerin.   Butyrate.

$$+ K.O.C_{16}H_{31}O + K.O.C_{18}H_{33}O.$$
Palmitate.   Oleate.
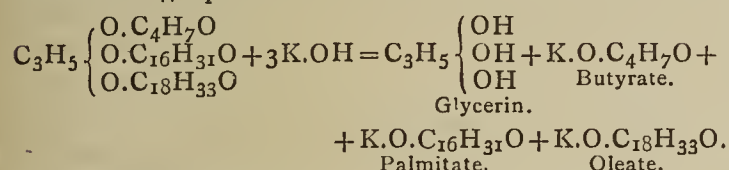
By treating butter-fat with only one-half the quantity of alcoholic soda necessary for its complete saponification, and diluting the liquid with water, Dr. James Bell obtained an oil which solidified at 4·4° C., and on saponification yielded 88·1 per cent of insoluble fatty acids, but no butyric or other soluble fatty acid. This result agrees with the formation of a di-glyceride of the following character, though it is to be regretted that no determination of the glycerin was made :—

$$C_3H_5 \begin{cases} O.H \\ O.C_{16}H_{31}O \\ O.C_{18}H_{33}O. \end{cases}$$
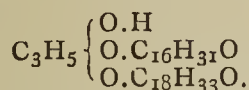
The products theoretically resulting from the saponification of natural fats and fatty oils, assuming them to have the constitution of triglycerides, will consist of from 94 to 96 per cent of fatty acids, and from 8·75 to about 13 per cent of glycerin, the usual proportion of the latter product being between 10 and 11 per cent.

The Isoglyceride Theory.

In 1883, Messrs. J. A. Wanklyn and W. Fox enunciated a new theory of the constitution of natural fats (CHEM. NEWS, xlviii., 49; "British Association Reports," 1883, p. 470; *Analyst*, iv., p. 73). The theory, which was very shortly stated, was simply that the accepted view, that the fats are ethers of glycerin, is only partially correct, and that instances of a different kind of structure occur among the natural oils and fats. According to the authors of the theory, the fats are in part composed of ethers of isoglycerin or homologues of isoglycerin. To the wholly hypothetical compound, isoglycerin, these authors attribute the formula $CH_3.CH_2.C(OH)_3$. This theoretical compound is assumed to exist only in its ethers, for

immediately on isolation it is imagined to be resolved into water and a fatty acid, thus :—

$$CH_3.CH_2.C(OH)_3 = CH_3.CH_2.COOH + H_2O.$$
Isoglycerin.   Propionic acid.   Water.

Of the existence of the isoglycerin with three carbon atoms absolutely no evidence has been attempted to be given ; but the authors consider that proof of the existence in butter-fat of ethers of the next higher homologue is afforded by the formation of ethyl butyrate when the fat is treated with an amount of alcoholic potash insufficient for its complete saponification. The formation of the ethyl butyrate they attribute to the decomposition of an isoglycerin containing C_4, this isoglycerin splitting up into butyric acid and water, and the nascent butyric acid reacting with the alcohol to form ethyl butyrate, thus :—

$$C_3H_7.C(OH)_3 = C_3H_7.CO.OH + H_2O ; \text{ and}$$
$$C_3H_7.CO.OH + C_2H_5.OH = C_3H_7.CO.OC_2H_5 + H_2O.$$
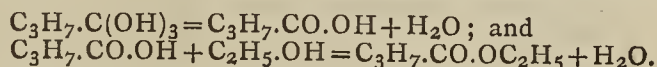
Wanklyn and Fox found that, under favourable circumstances, they could obtain from butter fat an amount of ethyl butyrate equivalent to fully 3 per cent of butyric acid, or about one-half of the total amount which can be isolated from saponified butter. Upon this single fact, coupled with a supposed serious deficiency in the amount of glycerin yielded when fats, and especially butter, are saponified, the authors erected their isoglycerin theory. But the reaction in question was some years since demonstrated by Mr. Hehner to be true also of synthetically prepared glycyl butyrate : besides which, I believe, Messrs. Wanklyn and Fox have never published a single original experiment in support of their assertion that the proportion of glycerin yielded by saponification of butter and other fats exhibits any grave departure from the amount required by the accepted view of their constitution,

In view of this omission, the isoglycerin theory might well have been allowed to remain at rest had it not recently been resuscitated by Mr. Wanklyn in a wholly unaltered form. Thus, at a recent meeting of the Society of Chemical Industry (*Journal*, x., p. 93), Mr. Wanklyn stated that "The evidence of the existence of the isoglyceride was that reaction (*i.e.*, the formation of ethyl butyrate), and the fact that one did not really get the theoretical quantity of glycerin from butter."

Mr. Wanklyn considers that the formation of ethyl butyrate, on heating butter-fat with a limited quantity of alcoholic potash, proves the existence of an isoglyceride, the isoglycerin of which splits up into butyric acid and water, the acid reacting with the alcohol to form ethyl butyrate. He contends that if the butyric acid were a primary product of the saponification of an ordinary glyceride, instead of a secondary product of the decomposition of an isoglycerin, it would not form ethyl butyrate, but potassium butyrate. It is certainly a curious and interesting fact that ethyl butyrate should be formed under any circumstances, seeing that it is readily converted by caustic potash into alcohol and potassium butyrate. But it must be remembered that the essential condition of its formation in notable amount, prescribed by Wanklyn and Fox themselves, is the use of the alkali in quantity insufficient to saponify the whole of the butter fat employed. The whole argument derived from the reaction falls to the ground in the face of the fact, demonstrated some years since by Mr. Hehner under the very noses of Messrs. Wanklyn and Fox (*Analyst*, ix., 76), that butyrin synthetically prepared by heating together butyric acid and glycerin, and thoroughly washing the product, developes abundance of ethyl butyrate when warmed with alcoholic potash !

The fact is that the reaction, which is regarded by Mr. Wanklyn as so anomalous, appears to be a perfectly normal and general one. Thus ethyl stearate may be actually prepared by boiling tristearin with a solution of sodium in absolute alcohol (Duffy), or *by heating tristearin with small quantities of alcoholic potash* (Bouis, *Compt. Rend.*, xlv., 35). Here, then, is the precise condition of success

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* A Paper read before the British Association, Cardiff Meeting, 1891, Section B.
† Mr. J. A. Wanklyn believes butter fat to contain some 40 per cent of the glyceride of a peculiar acid, which he names aldepalmitic acid, having the formula $C_{16}H_{30}O_2$.

in obtaining ethyl butyrate applied by Bouis to prepare the higher homologue.

P. Duffy (*Journ. Chem. Soc.*, v., 363) also obtained amyl stearate by boiling tristearin with a solution of sodium in amylic alcohol, and amyl palmitate by precisely similar means. When in the reaction of stearin and palmitin with amylate of sodium the proportion of the latter was increased beyond one equivalent, the quantity of ether obtained diminished, "with a quantity of sodium which was certainly not less than two equivalents, no ether was obtained."

Duffy further observed that when free stearic acid was substituted for stearin in the foregoing reaction, no ether was produced.

Experiments on Acetin.

It appears, therefore, that the glycerides of stearic, palmitic, and butyric acids each yield abundance of the ethyl salts of these acids when heated with alcoholic potash. To complete the chain of evidence and study the reaction more thoroughly, I have recently made a series of experiments, in conjunction with Mr. David Homfray, on acetin, the glyceride of acetic acid.

Some acetin was prepared by heating together 5 parts of glycerin with 6 of anhydrous sodium acetate and 15 of acetic anhydride. The mixture was kept boiling for an hour, in a flask furnished with a reflux condenser. It was then treated with water, and sodium carbonate added till the reaction was permanently alkaline, when the liquid was shaken with ether, which was separated, and the acetin recovered by distilling off the solvent.

One grm. of the acetin thus prepared was distilled with 30 c.c. of alcohol and 0·5 c.c. of alcoholic potash containing 80 grms. of caustic potash per litre. The distillate, which smelt strongly of acetic ether, was heated on the water-bath for half an hour with 10 c.c. of the same alcoholic potash solution (= 11·8 c.c. normal KHO), and the excess of alkali titrated back with standard hydrochloric acid and phenol-phthalein in the usual way. From this result we calculated the weight of acetic acid volatilised as acetic ether. The residue in the retort was treated with more alcohol and another 0·5 c.c. of alcoholic potash, the liquid distilled, and the distillate saponified as before. The following results were obtained, operating on 1 grm. of acetin in each case :—

		Alcoholic KHO employed. C.c.	Acetic acid in distillate. Per cent.	=	Acetin. Per cent.
a.	First distillate	0·5	53·4		65·12
	Second ,,	0·5	17·4		21·22
	Total	1·0	70·8		86·34
b.	First distillate	0·2	43·8		53·42
	Second ,,	1·0	26·4		32·19
	Total	1·2	70·2		85·60

The theoretical yield of acetic acid, supposing the whole of the substance employed to be pure triacetin and the conversion into ethyl acetate to have been complete, would be 0·826 grm. against 0·708 and 0·702 grm. actually produced.

A fresh quantity of acetin was next prepared, and an experiment made to ascertain if it volatilised with vapour of alcohol. 1·0848 grm. of acetin was distilled with 50 c.c. of alcohol, the distillate and residue both saponified, and the acetin calculated as before. In the distillate only 0·015 of acetic acid was found, while the residue contained 0·752 grm., the sum of the two being 0·767 grm. This result shows that the extraordinary results previously obtained were not due to actual volatilisation of acetin as such. The total yield of acetic acid is below the theoretical amount (0·826 grm.), doubtless owing to the presence of mono- or diacetin in the material employed. That it was not due to any error of experiment was proved by saponi-

fying a known weight of the acetin with excess of alcoholic soda $\left(\dfrac{N}{5}\text{ normal}\right)$ under a reflux condenser, and ascertaining the alkali consumed in the reaction by titration with standard acid and phenol-phthalein in the usual way. A yield of 76·03 per cent of acetic acid was obtained, as against 76·7 recorded above.

Another experiment was then made by distilling 1·135 grm. of the same specimen of acetin with 1·0 c.c. of $\dfrac{N}{5}$ normal soda and 30 c.c. of alcohol. The distillate was saponified with a known quantity of the same alcoholic soda, and titrated back with hydrochloric acid as usual. The residue in the retort was again distilled with alcohol and 1·0 c.c. of the same soda solution, and this treatment was repeated once more. The following are the figures obtained :—

		Alcoholic NaHO employed. C.c.	Acetic acid in distillate. Per cent.	=	Acetin. Per cent.
First distillate	..	1·0	32·19		39·02
Second ,,	..	1·0	26·22		31·97
Third ,,	..	1·0	11·00		13·41
Total	..	3·0	59·41		84·40

The volume of the caustic soda solution requisite to completely saponify the 1·135 grm. of acetin employed would be 50 c.c. Hence 1 c.c. of the alkaline solution is chemically sufficient to saponify only about *one-fiftieth* of the acetin used, and yet it causes the conversion of 39 per cent of it into acetic ether, while 3 c.c. converts 84·4 per cent.

Further experiments showed that the employment of a larger proportion of alkali diminished the yield of acetic ether ; thus with sufficient caustic soda to saponify 12·7 per cent of the acetin used, 85·2 per cent of the total acetic acid passed into the distillate as ethyl acetate. This, with the 12·7 remaining in the retort as sodium acetate, leaves only 2·1 per cent unsaponified or otherwise to be accounted for. In another experiment, in which the alkali used was equivalent to 39·8 per cent of the acetin, the amount converted into acetic ether was 52·4 per cent, leaving 7·8 per cent unaccounted for.

In all cases the distillates were found to be neutral to phenol-phthalein, showing that no free acetic acid had distilled over. The residues in the distilling flasks were always found to be slightly, but distinctly, *acid to phenolphthalein*, a fact which proves that the whole of the alkali employed invariably entered into reaction, and that some reaction occurred resulting in the production of free acetic acid. Hence it appears probable that the first action of the alkali on the acetin is to effect its hydrolysis, with formation of glycerin and free acetic acid. A portion of the latter then reacts with the alkali to form sodium acetate, while the greater part reacts with the alcohol to form ethyl acetate ; but a small proportion of the acetic acid fails to enter into this latter reaction, and hence remains in the free state in the distilling flask. Why the soda should effect the hydrolysis of a much larger amount of acetin than it can chemically react with is not clear ; but the behaviour of soda is evidently similar to that of lime, magnesia, and oxide of zinc, very small amounts of which (2 or 3 per cent) are found to very greatly facilitate the hydrolysis of fats by super-heated steam, and are largely employed with this object.

A few supplementary experiments deserve mention. 1 grm. of anhydrous sodium acetate was distilled with 50 c.c. of alcohol, the distillate boiled with alkali, and titrated back with standard acid, when it was found that no acetic ether had been formed. A mixture of acetin, alcohol, and anhydrous sodium acetate gave a small yield of acetic ether. It seemed possible that the result might be due to the presence of alkali in the sodium acetate. Hence the experiment was repeated by dissolving sodium acetate in alcohol, dropping in acetic acid till the alkaline

reaction to phenol-phthalein disappeared, then adding acetin and distilling as before. Acetic ether equivalent to 1·36 and 1·50 of the acetin taken was found in the distillate. This is no more than was obtained by distilling acetin and alcohol together.

The foregoing results appear to be so far-reaching in their consequences that I propose to investigate the subject more systematically than I have hitherto been able to do.

Duffy determined the glycerin produced by the saponification of the stearin he employed. The method of estimation consisted in evaporating the neutralised liquid resulting from the saponification nearly to dryness at a steam-heat, adding dry potassium carbonate, extracting the glycerin with absolute alcohol, filtering the solution, and evaporating the filtered solution in a vacuum until the residue was of constant weight. The glycerin thus found was corrected by the deduction of the ash left on ignition. By this process, which is likely to give low results, Duffy obtained 8·94 per cent of glycerin in two experiments, the theoretical yield from pure stearin being 10·34 per cent, a figure which does not leave much margin for the suggestion that the ethyl and amyl stearates were derived from an isoglycerin, which under the circumstances would have to be the member with 18 carbon atoms!

The process of estimating glycerin employed by Duffy was substantially the same as that described by Chevreul in 1823, by which the chemist isolated the following proportions of ash-free glycerin :—Human fat, 9·66 per cent ; pork, 8·82 ; beef, 8·60 ; mutton, 8·00 ; butter fat, 11·85; porpoise oil, 14·00. These results, with the exception of the two last, are sensibly below the theoretical yield, as might be expected from the process employed. Further, the statement made by Mr. Wanklyn that manufacturers never obtain more than 5 per cent of glycerin on saponifying fats, is contrary to the experience of some of the largest firms, who *recover* 7·5 to 8 per cent, and take no notice of the considerable loss of glycerin by evaporation during the process of concentration, besides which the process of saponification is often far from complete.

To come to more recent determinations of glycerin in fats, Mr. Hehner has published the following figures, obtained by boiling the leys from the saponification with a dilute acid solution of potassium bichromate, and ascertaining the excess of oxidising agent by titration with a ferrous salt (*Analyst*, xii., 44).

Now this process is not open to the objection which has been raised against some, for it has recently been stated by a coadjutor of Mr. Wanklyn (*Journ. Soc. Chem. Ind.*, x., 204) that dilute chromic acid mixture remains practically unchanged when boiled with butyric acid, and further (*Analyst*, xvi., 30), that butyric acid is the only soluble non-volatile fatty acid to be detected in the glycerin mother-liquor obtained by the saponification of butter fat.

The following are figures obtained by Mr. Hehner by the bichromate titration process :—

Fat.	Glycerin.
Olive oil	10·26 per cent.
Cod-liver oil.. ..	9·87 ,,
Linseed oil	10·24 ,,
Margarine	10·01 ,,
Butter fat	12·40 ,,

As already pointed, it is a curious fact that the authors of the isoglyceride theory have not, to my knowledge, published any experiments in support of their assertion that butter, tallow, and other fats yield on saponification little more than half the theoretical proportion of glycerin. This is the more curious since a valuable method of determining glycerin in fats was originally suggested by Mr. Wanklyn and further worked out by Mr. Fox (*Oil and Colour Journ.*, v., 1402 ; CHEMICAL NEWS, liii., 15) and Benedikt and Zsigmondy (*Chem. Zeit.*, ix., 975; *Analyst*, x., 206). The method is based on the oxidation of the glycerin by treatment with permanganate in pre-

sence of excess of caustic alkali, whereby it is converted into oxalic acid, carbon dioxide, and water, in accordance with the equation, $C_3H_8O_3 + 3O_2 = C_2H_2O_4 + CO_2 + 3H_2O$. The excess of permanganate is destroyed by a sulphite, the filtrate acidulated with acetic acid, and the oxalate precipitated as a calcium salt.

This process has been very fully investigated in my laboratory by Mr. J. C. Belcher, and proved to give very accurate results in the absence of foreign bodies yielding oxalic acid by oxidation. Alcohol is one of these, and hence, to avoid all risk of its presence, I have described a method of saponifying the substance with aqueous potash (*Analyst*, xi., 52 ; "Com. Org. Analysis," ii., 290). This modification and careful proof by experiment that oxalic acid is not acted on by permanganate in strongly alkaline solution, is the extent of my responsibility for the process in question (*Jour. Soc. Chem. Ind.*, x., 204).

Benedikt and Zsigmondy, however, proved by experiment that the soluble fatty acids of oils, such as acetic, butyric, caproic, &c., do not, on treatment with alkaline permanganate, yield any acids the calcium salts of which are precipitated from acetic solutions, and hence are liable to be mistaken for calcium oxalate. The higher fatty acids of the stearic series are insoluble in water, and hence would not in any case interfere. On the other hand, certain acids of the acrylic or oleic series, and possibly oleic acid itself, yield oxalic acid by oxidation with permanganate. The higher acids of the oleic series are, however, insoluble in water, and the lower are not known to occur in fixed oils under normal conditions. Under certain circumstances, however, the method is wholly invalidated, as I found when attempting to apply it to the examination of oxidised linseed oil.

The following tabulated statement of results obtained by the alkaline permanganate process of estimating glycerin is taken from vol. ii. of my "Commercial Organic Analysis," page 33 :—

	Glycerin per cent.	
Kind of Fatty Oil.	Benedikt and Zsigmondy.	Allen.
Northern whale oil		11·96
Porpoise oil..		11·09
Menhaden oil		11·10
Lard		10·83
Tallow	9·9—10·0	—
Butter fat	10·2—11·6	11·06
Olive oil	10·1—11·4	—
Linseed oil	9·4—10·0	9·39
Castor oil		9·13
Cocoa-nut oil	13·3—14·5	12·11
Palm-nut oil		11·70
Palm oil (containing much free acid)		9·71

Behaviour of Butyric Acid with Alkaline Permanganate

The applicability of the alkaline permanganate process to the estimation of the glycerin from butter has been recently denied by W. Johnstone (CHEMICAL NEWS, lxiii., 111 ; *Analyst*, xvi., 49; *Jour. Soc. Chem. Ind.*, x., 204) on the ground that butyric acid itself yields oxalic acid on treatment with alkaline permanganate in the manner described by Benedikt and Zsigmondy for the estimation of glycerin. The same authority states (*Analyst*, xvi., 30) that butyric acid is the only soluble non-volatile acid he could detect in the glycerin mother-liquor from the saponification of butter, and he also states that the oxalic acid yielded is equivalent to from 11·7—12·23 per cent of glycerin (*Jour. Soc. Chem. Ind.*, x., 93). The effect of alkaline permanganate on butyric acid is stated to be to oxidise it to oxalic acid in accordance with the following somewhat eccentric equation (CHEMICAL NEWS, lxiii., 111 ; *Jour. Soc. Chem. Ind.*, x., 204) :—

$$C_4H_8O_2 + O_6 = 2C_2H_2O_4 + H_4.$$
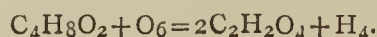
Dr. William Johnstone, the discoverer of this reaction, quotes two experiments on pure butyric acid by which he obtained amounts of oxalic acid corresponding to 93·64 and 94·07 per cent of the butyric acid taken. This result is of so remarkable a nature, and so completely opposed to the experience of Benedikt and Zsigmondy and all previous observers, that one is disposed to receive it with some reserve, especially as the same observer recently published experiments (*Analyst*, xvi., 26), according to which tallow requires 23 per cent of caustic potash (KHO) for its saponification, against 19·3—19·8 per cent as the united experience of numerous other observers; that butter fat requires about 27 per cent of potash against the general experience of 22·1—23·3 per cent; and detailing other analytical results of an equally remarkable character.

As, however, the observer in question makes the distinct assertion, as the result of experiment, that butyric acid is oxidised to oxalic acid by alkaline permanganate, and hence that the estimation of glycerin in butter by the same process is invalidated, and considerable support thereby given to Mr. Wanklyn's isoglyceride theory (*Jour. Soc. Chem. Ind.*, x., 204), I have thought it right to ascertain by actual experiment whether the statement in question had any foundation in fact. That it was erroneous was already rendered extremely probable by Mr. Hehner's failure to obtain any trace of oxalic acid from butyric acid by treatment with permanganate (*Analyst*, xvi., 49).

In order to settle the point in question beyond the possibility of further cavil, 20 grms. of butter fat were saponified by heating it for six or eight hours to 100° C. in a closed bottle with a solution of 8 grms. of caustic potash in 50 c.c. of water. The soap obtained was dissolved in hot water, and decomposed by dilute sulphuric acid in quantity sufficient to convert the potash into $KHSO_4$. The liquid was then allowed to become cold and poured off through a filter from the cake of insoluble acids. The latter was washed by boiling with water, the washings when cold being filtered and added to the main solution. This solution, containing the glycerin and soluble fatty acids resulting from the saponification, was then distilled to a small bulk, water added, and the liquid again distilled to a small volume.

The distillate was then oxidised by alkaline permanganate in the usual way. The reduced and filtered liquid gave *no trace of precipitate* when acidulated with acetic acid and treated with calcium chloride, showing that *no oxalic acid had been formed from the butyric acid*, and that *no glycerin* had distilled over.

The residual liquid remaining in the distilling flask was divided into four equal portions. Nos. 1, 2, and 3 were oxidised by respectively a slight excess, a moderate excess, and a large excess of alkaline permanganate, by which quantities of oxalic were formed equivalent respectively to a production of 11·12, 11·52, and 11·78 per cent of *glycerin* by the saponification of the butter fat. The fourth portion of liquid was exactly neutralised by caustic potash, concentrated, cooled, and filtered from the potassium sulphate which crystallised out. The filter was washed with alcohol, and more alcohol added to the filtrate as long as a precipitate was produced. The liquid was filtered and evaporated on the water-bath till the residue was nearly constant in weight. The residue, which was syrupy and had the characters of glycerin, was ignited and the ash deducted from the weight previously observed. A direct determination of the *glycerin* by weight in this manner showed 11·22 present.

Other estimations of glycerin by the same process, but employing 20 grms. (instead of 5 grms.) of butter fat gave 10·77, 11·53, and 12·15 per cent of ash-free *glycerin.*

In another experiment 20 grms. of butter fat was saponified with aqueous potash, the soap decomposed with acid, and the acid liquid divided into two equal portions, *A* and *B*.

A was distilled to a small bulk as before, and the residue in the flask divided into two equal portions.

| No. 1 showed by oxidation with alkaline permanganate 11·52 p.c. of glycerin. | No. 2 gave Mr. Hehner by the bichromate oxidation-method 11·83 p.c. of glycerin. |

B was divided into two equal parts without previous distillation to separate butyric acid.

| No. 3 showed with alkaline permanganate 10·86 per cent of glycerin. | No. 4 was lost. |

The foregoing experiments were made in my laboratory by Mr. D. Homfray, to whom my best acknowledgments are due. The experiments appear to prove:—

1. That butyric acid does not yield oxalic acid when oxidised by alkaline permanganate in the manner prescribed by Benedikt and Zsigmondy.

2. That the amount of oxalic acid formed by oxidising by alkaline permanganate the soluble products of the saponification of butter, is not greater when the oxidation is effected in presence of the butyric acid than when that acid is previously removed by distillation.

3. That the oxalic acid produced by the permanganate treatment corresponds to a formation of 11 to 12 per cent of glycerin from the butter fat saponified.

4. That this result is fully confirmed by actual isolation and weighing of the glycerin resulting from the saponification.

5. That there is no foundation for the isoglyceride theory so far as butter fat is concerned.

A NEW QUANTITATIVE SEPARATION OF MANGANESE AND ZINC.

By PAUL JANNASCH and J. F. McGREGORY.

THE process depends on the ready and complete conversion of the former metal into insoluble manganese hyperhydroxide by the action of hydrogen peroxide in an alkaline solution, whilst compounds of zinc, if present, remain unaffected. Carnot was the first who precipitated manganese salts alone by the above reagent, and thus determined their manganese quantitatively.

As one of the writers made numerous preliminary experiments more than two years ago on the oxidising action of hydrogen peroxide, and in developing his new method for the determination of sulphur in inorganic sulphides, found that it was a remarkably efficient oxidising agent, he thought it well not to delay any longer to institute a series of quantitative separations by means of hydrogen peroxide. The first of these results, the separation of zinc and manganese, executed in concert with Prof. McGregory, is here communicated.

In our first experiments we proceeded with solutions of the mixed sulphates acidified with dilute hydrochloric acid, adding next a moderate excess of concentrated ammonia, and then heating the precipitation with hydrogen peroxide for some time on the water-bath. Considerable quantities of zinc oxide were regularly found mixed with the precipitate of manganese. In one case where the precipitate had stood covered on the water-bath for more than four hours, the manganese separated was found to contain 0·0822 grm. ZnO (the quantities employed having been 0·5380 grm. $MnSO_4,5H_2O$, and 0·5602 grm. $ZnSO_4,7H_2O$). That precipitation of zinc was occasioned by the expulsion of the excess of ammonia on the water-bath was learnt from the solutions filtered off from the manganese precipitate, which, on evaporation, soon be-

came turbid by the separation of a white flocculent deposit which was subsequently re-dissolved.

As we afterwards heated on the water-bath for a very short time only, the results obtained were considerably better, so that on the average the proportion of manganous oxide was found too high by 2·5 per cent, which excess could be reduced by 0·5 per cent by washing the precipitate with dilute ammonia. The results obtained became perfectly satisfactory only when we considerably increased the proportion of the ammonium chloride and ammonia in the liquid to be precipitated, and proceeded finally exactly as follows :—A mixture of 0·5 grm. manganese sulphate and 0·5 grm. zinc sulphate were dissolved in 75—100 c.c. of water in a capsule of Berlin porcelain capable of conveniently holding 600 c.c., and the solution was acidulated with a little dilute hydrochloric acid. A considerable quantity of a 15—20 per cent solution of sal-ammoniac (at least 100 c.c.) was added, and lastly the liquid was made strongly alkaline by the addition of 60—100 concentrated ammonia, when no brownish colouration of manganese hydroxide must appear. The solution thus prepared and covered with a glass capsule is immediately mixed with an excess (50—60 c.c.) of pure hydrogen peroxide (*Hydrogenium peroxydatum puris* from H. Trommsdorff, of Erfurt, and perfectly free from barium chloride), which at once completely precipitates all the manganese. The mixture is then heated for 10—15 minutes on a boiling water-bath until the precipitate subsides perfectly, when it is collected on a capacious filter. Any residue adhering to the porcelain is removed by means of a goose-feather, suitably trimmed, rinsed out of the capsule by means of hot water and a little ammonia. The precipitate is washed with boiling water, slightly ammoniacal, and at last with hot water alone, until a drop of the filtrate, if evaporated on platinum foil, leaves no residue. The precipitate of manganese may be incinerated while still moist in a platinum or porcelain crucible, and ignited in the blast flame until the weight is constant. A repetition of the precipitation is quite superfluous, and it is not necessary to dissolve the precipitate in hydrochloric acid in order afterwards to precipitate the manganese as a carbonate.

For determining the zinc in the filtrate which has thus been freed from carbonate there is the choice of two methods. In the former, the boiling ammoniacal solution is precipitated with ammonium sulphide, and the precipitate of zinc sulphide is heated for an hour on the water-bath and filtered.

As the precipitate of zinc sulphide cannot be washed without inconvenience, owing to its clogging the filter and running through turbid, it is better to pass only the liquid in the beaker through the filter, then to return the latter with the unwashed precipitate into the beaker, and re-dissolve the precipitate in dilute hydrochloric acid with the aid of heat, so that the precipitation of zinc may be effected by sodium carbonate in presence only of a trifling quantity of ammonium salt. It must be remembered that zinc carbonate if thus precipitated may be contaminated with a little silica.

The second method is equally accurate and more rapid. The solution of zinc is evaporated to dryness in a large platinum capsule on the water-bath (stirring towards the end is not necessary) ; the residual saline mass is heated for about an hour on an air-bath to 125—150°, and the ammoniacal salts are driven off by heating more strongly on an asbestos capsule over the gas flame. The saline masses left adhering to the sides of the capsule are pushed down to the bottom by means of a stout platinum wire. The expulsion of the ammoniacal salts by direct heating over the naked flame is not admissible, as particles of zinc might be lost. The non-volatile residue is dissolved in hot water and a couple of drops of hydrochloric acid, the solution is filtered, and the filtrate, whilst boiling, is precipitated with sodium carbonate.

The authors are already in a position to assert that manganese, nickel, and probably cobalt, may be separated in a similar manner. They are further studying the behaviour of the alkaline potassium cyanide solutions of cobalt, nickel, and manganese with hydrogen peroxide.— *Journ. fur Prakt. Chemie.*

CONTRIBUTIONS TO MICRO-CHEMICAL ANALYSIS.*

By H. BEHRENS.
(Concluded from p. 174.)

L.—*Tellurium.*

1. MAGNESIUM throws down, from acid solutions of tellurium dioxide, films and scales of tellurium which appear of a dark greyish brown by transmitted light. Selenium is masked, even if present in considerable quantity. On the other hand, arsenic masks tellurium. The limit of the reaction is at 0·006 m.grm. Te.

2. Cæsium chloride precipitates from solutions of tellurium dioxide a hydrochloric acid yellow octahedra of 10—30 micro. Chloro-tellurite is distinguished from chloro-platinate by the size of its crystals and its behaviour with water. The crystals are rendered turbid by water, from which they cannot be re-crystallised, though they can from hydrochloric acid. Potassium iodide covers them black. The limit of the reaction is at 0·0003 m.grm. Te.

3. Potassium iodide occasions no change in alkaline solutions of tellurium dioxide. On the addition of hydrochloric acid a yellow and brown colouration appears, and there are deposited opaque rhombs, hexagons, and rods of 10—20 micro., which appear of reddish brown by reflected light. The reaction has its limits at 0·0006 m.grm. Te, and in presence of bismuth it is worthless.

From solutions containing selenium and tellurium, potassium iodide precipitates first tellurium iodide and afterwards red selenium iodide. If tellurate and selenite were in solution, selenium iodide is thrown down only after heating with hydrochloric acid. Selenium iodide may also be recognised by sublimation, as it is volatilised at a lower temperature than tellurium tetraiodide.

LI.—*Molybdenum.*

1. Sodium phosphate, after supersaturation with nitric acid, throws down yellow phospho-molybdate from solutions of molybdic acid in potassa or ammonia. Compare Potassium 2. Care must be taken that there is no excess of sodium phosphate in the liquid as it has a solvent action upon the insoluble phospho-molybdates. By proceeding cautiously 0·0001 m.grm. of Mo can be recognised in this manner. Thallous phospho-molybdate has a more intense colour, and forms smaller crystals than the potassium salt. It adheres firmly to the glass, and is therefore suited for separating and concentrating molybdenum, the rather as it can be converted into the compound mentioned under No. 2 of Potassa or Soda.

2. Thallous sulphate determines, in solutions of molybdic acid which contain free alkali, the separations of colourless, reflecting, hexagonal leaflets of 30—60 micro., which are so thin that by reflected light they show bright interference colours from blue-grey of the first order to green of the second. By the side of the leaflets and upon them there appears sometimes an elegant network of thin reflecting rods. In both cases we have probably to do with Oettinger's molybdate, Tl_2MoO_4. The limit of this fine reaction is at 0·000033 m.grm. Mo ; the limit of immediate precipitation is at a 5000 times dilution of molybdic acid.

It is most convenient to place a granule of thallous sulphate in a solution which contains 0·1 per cent of molybdic acid and a small excess of caustic soda. The leaflets form then a fringe round the reagent. They are

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* *Zeit. Anal. Chemie,*

soluble in hot water, but are not improved by re-crystallisation. Nitric acid destroys them rapidly, and if phosphoric acid is present yellow phospho-molybdate is deposited. On the other hand, thallous phospho-molybdate is converted by caustic soda into the compound here described.

LII.—*Tungsten.*

1. The yellow colour of precipitated tungstic acid appears most distinctly when the white hydrate is heated with hydrochloric acid. The most essential condition is a compact state of the precipitate. Light flakes and fine dust assume merely a yellowish tint. On this account the precipitate does not succeed with less than 0.01 m.grm. WO_3. If it is not practicable to distinguish the yellow colour, the unequal solubility of molybdic and tungstic acids in nitric acid may serve for isolating and recognising the latter compounds. In this manner we may separate 0.002 m.grm. WO_3. It is repeatedly evaporated down with strong acid, and then extracted in hot dilute acid. The limit of precipitation is at 0.0016 m.grm. W.

2. Sodium phosphate throws down from solutions of potassium and sodium tungstate, on the addition of an excess of nitric acid, colourless crystals of phospho-tungstate agreeing in form and shape with those of the phospho-molybdates. In solutions containing both molybdenum and tungsten there appear mixed crystals, the colour of which depends on the proportion of molybdenum. The limit of the reaction is at 0.00012.

3. Thallous sulphate gives, in alkaline solutions of tungstic acid, crystalline leaflets which may extend to 400 micro., but are in other respects exactly similar to those of thallous molybdate. If heated with nitric acid and sodium phosphate they are converted into colourless phospho-tungstate. The limit of the reaction is at 0.00008 m.grm. W.

LIII.—*Uranium.*

1. Sodium acetate precipitates, from neutral and faintly acid solutions of uranium, light yellow tetrahedra of uranyl acetate, which have been already mentioned under Sodium 1. The limit of instant reaction is between 1 and 0.5 per cent of uranyl acetate. Beyond this limit the reaction may be masked by other crystalline salts. In solutions which contain only uranium salt the reaction may extend to 0.0006 m.grm. U.

2. Thallous sulphate effects, in ammoniacal solutions of uranyl carbonate, the separation of clear pale yellow rhombs of 30—70 micro. in length. They display strong polarisation and right extinction. This reaction loses nothing of its distinctness if the uranyl salt is diluted 5000 times. Sodium carbonate may be used instead of the ammonium carbonate, but the rhombic crystals are the less simple and well developed. The limit of this reaction is at 0.0001 m.grm. U.

LIV.—*Chlorine.*

1. Thallous sulphate precipitates, from solutions of chlorides, small, colourless, strongly refractive cubes. Compare Thallium 1. Instead of thallous sulphate, lead acetate may be used, but the sensitiveness is then reduced to 0.0005 m.grm. Cl, and the long spiculæ of lead chloride are not particularly characteristic. With thallous sulphate 0.0001 m.grm. chlorine may be recognised.

2. Silver nitrate throws down a curdy precipitate of silver chloride, which may be obtained in crystals by solution in ammonia or in hot hydrochloric acid. Compare Silver 1. The limit of the reaction is at 0.00005 m.grm. Cl.

3. Platinic sulphate renders the reaction by twenty times more sensitive. We test first with thallous sulphate, and if no reaction ensues we add platinic sulphate. Excess must be avoided, so as not to obtain crystals of double sulphates. Compare Thallium 3. The reaction detects 0.000004 m.grm. Cl.

4. If potassium sulphate or nitrate is used along with

platinic sulphate we obtain no greater sensitiveness than with salts of lead, but there are formed large crystals of potassium platinum chloride (compare Potassium 1), and the possibility of simultaneously detecting chlorine and bromine. (See Bromine.)

LV.—*Bromine.*

1. The reagents 1, 2, and 3 for chlorides give with bromides reactions which can only be distinguished from those described under Chlorine 1, 2, and 3, by the smaller size of the crystals. The limit of the reaction with thallous sulphate is 0.00016 m.grm. Br; with silver nitrate and ammonia, 0.00005 m.grm. Br; with thallous sulphate and platinic sulphate, at 0.000006 m.grm. Br.

2. With platinic sulphate and potassium nitrate we obtain, in solutions of bromides, orange-red octahedra of potassium platinum bromide *prior* to the appearance of the platinum chloride, which chiefly crystallises out at the margin of the drop. Here also an excess of the reagents must be avoided. The limit of the reaction is 0.00024 m.grm. Br. Instantaneous reaction is obtained down to 0.3 per cent potassium bromide.

3. If a little gold chloride is added to a solution containing not too little bromide, and if a granule of thallous sulphate is added, bromo-aurate crystallises out first. Solutions with 1 per cent potassium bromide yield an orange-red powder, which dissolves on heating. At the margin of the drop massive orange prisms then crystallise out. The heating must not be pushed too far, and caution must be used in the addition of the gold chloride in order to obtain as little chloro-aurate as possible. The limit of the reaction is at 0.0007 m.grm. Br; the limit of instantaneous action is at 3.0 per cent potassium bromide.

4. If we place in a liquid containing a bromide a few granules of starch, acidulate with sulphuric acid, and add finally a little potassium nitrite, the starch granules assume a colour varying from light yellow to orange-yellow. With solutions which contain less than 0.2 per cent of potassium bromide we have to wait some minutes for the appearance of the colour. In this case it is advisable to cover the preparation with a flat watch-glass. As a matter of course caution must be used with the addition of the nitrite if chlorides are present. The reaction is exceedingly characteristic, but unfortunately not as sensitive as it might be desired. The limit lies at 0.02 m.grm. Br.

LVI.—*Iodine.*

1. Thallous sulphate and silver nitrate give yellow precipitates in solutions of iodides, which cannot readily serve for detecting iodine in presence of bromine. In case of need thallous bromide can be extracted by boiling in water, and silver bromide by treatment with ammonia in the cold. The limit of the precipitation for thallous sulphate is at 0.00017 m.grm. I; silver nitrate is not more sensitive, as the solution of silver iodide in ammonia does not yield characteristic crystals.

2. Palladium nitrate occasions in solutions of iodides, even if very dilute, a flocculent black-brown precipitate. Compare Palladium 1. The limit of the reaction is at 0.0001 m.grm. I. If bromine is present palladium chloride is used instead of the nitrate.

3. Platinic sulphate colours solutions of iodides a vinous red, and separates out black, pulverulent, platinum iodide. If potassium salts are present the separation of platinum iodide may not take place; there appear octahedra of platinum-potassium iodide, resembling graphite in colour, and of the same size as those of the chloro-platinate; they appear first, *before* the orange-red crystals of the bromo-platinate. The limit of the reaction is at 0.0002 m.grm. I; the limit of immediate reaction is at the 800-fold dilution of potassium iodide.

4. Mercuric chloride precipitates iodides of a scarlet colour. The reagent is characteristic and convenient, as an excess of the reagent is not injurious. Compare

Mercury *b*, 1. The limit of the reaction is 0·0002 m.grm. I.

5. Starch is coloured by free iodine an intense blue; the process is the same as that described under Bromine 4. If much sulphuric acid is added the colour of the iodised starch grows paler after some time, and becomes a vinous red. The limit of this very characteristic reaction is at 0·00017 m.grm. I. If bromine is present along with iodine, the colour of the starch occasioned by the latter may be easily masked. The blue colour is alone perceptible, and it must be destroyed before the reaction of the bromine is visible. This can be easily effected by the addition of hydrochloric acid and a particle of potassium chlorate. In the vicinity of the latter the starch granules are decolourised, or, if bromine is present, turned yellow to orange. Subsequently the yellow colour disappears here, but becomes more distinct at a greater distance.

LVII.—*Fluorine.*

1. Sodium chloride is to be recommended as a precipitant whenever it is necessary to distil off fluorine as silicon fluoride. Compare Silicon 1. Ths limit of the reaction is then at 0·002 m.grm. F. Fluoriferous silicates which are not decomposed by sulphuric acid are prepared by fusion with soda and evaporation with acetic acid. If no distillation is needed the limit is at 0·00004 m.grm. F.

2. Barium salts yield a silico-fluoride less characteristic in form (compare Barium 2), but react three times more sensitively than sodium chloride. In the most favourable base the limit with barium chloride is 0·000015 m.grm. F.

ON A COMBINATION OF WET AND DRY METHODS IN CHEMICAL ANALYSIS.*

PART I.

By W. E. ADENEY, F.I.C., Assoc.R.C.Sc.I., Curator, Royal University of Ireland; and T. A. SHEGOG, A.I.C., Assoc.R.C.Sc,I., Assist. Chemist, Royal College of Science, Dublin.

Details of Manipulation.

The Charcoal Support.—The pieces should be from 12 inches to 18 inches in length, and from 1½ inches to 2 inches in diameter, and must be tolerably free from fissures. Our first experiments were made with charcoal of a very fair quality got from Messrs. Griffin and Son, of London. Later on, some of excellent quality was obtained from Messrs. Harrington Bros., of Cork.

The cavity into which the substance is to be introduced should be bored in the end of the stick of charcoal, and its size and shape are of importance. In shape it should be conical, the sides being slightly curved. The dimensions most convenient for the quantities we dealt with were—diameter, 1¼ inches; greatest depth, 1½ inches. If the cavity be much larger or smaller than this, the charge cannot be worked about in the proper manner. The ratio of diameter to depth should be attended to, for if the hole be too deep in relation to its diameter, the flame will be blown back, and the charge cannot be properly heated.

The Source of Heat.—In our earlier experiments a lamp which burnt solid paraffin was used. This had the advantages of being very portable and not likely to get out of order. Later on an ordinary paraffin oil lamp was employed; but, although either of these lamps will answer perfectly, we found that when coal gas is procurable it is by far the most convenient source of heat. It can be burnt at the end of a flattened tube, and if the tube be pivoted so that it can rotate in a vertical plane it will be found of advantage in dealing with easily oxidisable metallic beads, as will be explained later.

The blowpipe used was an ordinary mouth blowpipe, furnished with a platinum jet, and fixed in a clip on a retort-stand. An indiarubber hand blower was used for obtaining the blast.

The borax used was fused in a platinum dish and powdered. It should be kept in a dry and well-stoppered bottle.

The silver was at first fused in the form of nitrate, but the troublesome deflagration which took place when this salt was heated soon led to its use being discontinued. Silver chloride, mixed with the substance and borax before fusion, was next tried, and was found to work very satisfactorily. Subsequently it was found that with substances of a certain type, the most satisfactory results were obtained when the substance and fluxes were first fused together in a shallow cavity in charcoal, the oxidising flame being employed. When fusion was complete the mass was allowed to cool, transferred to a cavity of the usual size and shape in a fresh piece of charcoal, the silver added in the form of wire or in a button, and the fusion continued in the reducing flame. Experiments were also made in which silver oxide was used instead of silver chloride, but no advantage was apparent. In some cases, when dealing with metals which form infusible alloys with silver, lead was added, either as litharge or as metal. The results obtained were not satisfactory, but this requires further working out.

The form in which the silver should be added depends on the nature of the substance. If the substance consist mostly of compounds of lead, bismuth, copper, arsenic, antimony, or tin, silver chloride should be employed, and should be mixed with the substance and borax before the fusion. If, however, the substance consist principally of difficultly reducible oxides or oxides of nickel or zinc, then metallic silver, added after fusion, is best.

In some cases the substance and fluxes were fused together in a shallow cavity, using the oxidising flame; cooled, powdered in an agate mortar, then mixed with silver chloride, and again fused. This is very troublesome, and the employment of the silver as wire was found to give quite as good results.

The sodium carbonate used was the ordinary dried and powdered material. After a great number of experiments its employment was discontinued, except when dealing with siliceous substances, as no advantage seemed to attend its use with other bodies.

Quantities.—The most convenient quantities to work upon generally are 3 decigrms. of substance, and 12 decigrms. of borax. These quantities yield beads which can be easily worked before the blowpipe in the necessary manner, in a cavity of the dimensions given above. The proportion of borax may be varied within reasonable limits (from two to six times the weight of substance taken) without injuriously affecting the fusion. In dealing with a body containing very large proportions of nickel or zinc, not more than 1 decigrm. of the substance should be taken.

While the fusion is proceeding, the charge must be worked round and round the cavity, the metal bead being made to run round the glass, and pick up the metals as reduced. When finished the whole charge may be allowed to sink to the bottom of the cavity, the metal bead being under the glass. This somewhat protects the metals from oxidisation.

The fusion must be cooled most carefully in an atmosphere of coal gas (by directing a stream of gas into the cavity), as otherwise some easily oxidisable metals may become oxidised. This is especially necessary when arsenic, lead, bismuth, tin, or zinc are present.

We found that the compounds of nickel, cobalt, iron, zinc, and tin, with phosphoric acid and silicic acid, behave before the blowpipe in a similar manner to the salts of these metals with volatile acids.

DIFFICULTLY REDUCIBLE METALLIC OXIDES.

Iron, Chromium, Aluminium, Cobalt, and Manganese.

Experiments were made with the compounds of the above-mentioned metals, as with the compounds of the

FIRST SERIES OF EXPERIMENTS.

(Silver Chloride Mixed with the Substance and Fluxes before Fusion).

EASILY REDUCIBLE METALLIC OXIDES.

Metal.	Quantities of Fluxes and substance.	Deci-grms.	Reduction.	Remarks.
1. Antimony	Tartar emetic	3	Practically complete.	Fusion went well, both beads easily fusible. Assay was cooled in stream of coal-gas. A very slight trace of antimony was found in glass bead.
	Bicarbonate of soda..	3		
	Borax..	12		
	Silver chloride.. ..	12		
2. Tin	Stannic oxide	3	Incomplete.	Tin in fair quantity was found in both beads. Both beads were easily fusible. In another experiment silica was added, but without beneficial result.
	Bicarbonate of soda..	3		
	Borax..	6		
	Silver chloride.. ..	12		
3. Lead ..	Lead acetate crystals	3	Complete.	Both beads easily fusible. Assay was cooled in coal-gas. On testing glass bead, no lead was found. With lead, the whole assay must be kept covered with a good reducing flame during the entire fusion.
	Bicarbonate of soda..	3		
	Borax..	6		
	Silver chloride.. ..	12		
4. Arsenic ..	Arsenic trioxide ..	1	Complete.	It will be noted that the proportions used are the same as those usually employed. The actual weights were taken small, as it was feared that the volatilisation of arsenic might be troublesome. This, however, was not found to be the case: the volatilisation was very slight, and was confined to the beginning of the fusion. The fusion went easily; the assay was cooled in coal-gas. No arsenic was found on testing the glass bead, but a large quantity was found in the metallic bead.
	Bicarbonate of soda..	1		
	Borax..	4		
	Silver chloride.. ..	4		
5. Silver ..	Silver nitrate	3	Complete.	Great difficulty was experienced in getting a fusible metallic bead. The glass bead, on cooling, became in parts white and opaque, and small quantities of metallic scale came up on its surface. On testing the glass bead, no silver was found.
	Borax..	12		
6. Bismuth ..	{ Bismuth nitrate crystals..	1 }	Complete.	Metallic bead was very easily fusible. On testing the borax bead, no bismuth was found.
	Bicarbonate of soda..	2		
	Borax..	6		
	Silver chloride.. ..	8		
7. Copper ..	{ Copper sulphate crystals..	3 }	Complete.	This fusion was gradually heated. The assay was cooled in coal-gas; the glass bead obtained was clear and transparent. The borax bead was tested for copper, but none was found. Experiments were tried, in which varying quantities of litharge were used instead of silver chloride, but the reduction was in all such cases incomplete.
	Bicarbonate of soda..	3		
	Borax..	12		
	Silver chloride.. ..	12		
		Centi-grms.		
8. Nickel ..	Nickel chloride . ..	5	Complete.	With these small quantities the fusion went very well, both beads being sufficiently fusible. On testing the borax bead for nickel, none was found present. With larger quantities the results were not satisfactory. Other experiments were made without the use of arsenic, but in all cases the greatest difficulty was experienced in getting a fusible bead, even when the proportion of silver chloride to nickel chloride was 1 to 40. Litharge was tried instead of silver chloride, but though a fusible bead resulted, the fusion was not a success.
	Borax..	15		
	Metallic arsenic ..	15		
	Silver chloride.. ..	10		
		Deci-grms.		
9. Zinc . ..	Zinc sulphate	3	Incomplete.	Both beads were very easily fusible. The metallic bead tailed like impure mercury, and was more fusible than the glass bead. The amount of arsenic volatilised was inconsiderable. The assay was cooled in coal-gas. On testing, zinc was found in both beads. Other experiments were made without the use of arsenic, but the metallic bead was infusible in all cases except where litharge was employed. In some experiments silica was added to the charge, but without good result.
	Bicarbonate of soda..	3		
	Borax..	6		
	Metallic arsenic ..	1·5		
	Silver chloride.. ..	12		

NOTE.—The experiments tabulated above are those which we regard as having given the most satisfactory results in each case.

easily reducible oxides. The results were somewhat surprising. In each case, the silver immediately on reduction, became infusible, or very difficultly fusible, but on heating the reduced silver for a long time, with the tip of a good oxidising flame, it could in all cases be made fusible.

Under the conditions of the experiment, it was thought probable that these metals were, at least to a small extent, reduced. It seemed to us possible that a small quantity might become reduced before the substance could be dissolved in the borax ; and if this occurred we should expect the alloy formed to be infusible or difficultly fusible.

To avoid such possible reduction, the substances were first fused with borax alone on charcoal, in the oxidising flame, the glass bead was then powdered, mixed with the silver chloride, and heated in the reducing flame ; the results was not more satisfactory, the metallic bead in each case became infusible soon after reduction. It was found that small quantities of iron and cobalt were reduced even when their compounds were heated with borax alone in the oxidising flame, the reduced metal was always found as a thin film or small globules on that surface of the glass which had cooled in contact with the charcoal. In each of these experiments the weight of substance taken was 3 decigrms., and of borax 12 decigrms.

Some experiments were next made with cobalt chloride to. ascertain whether by decreasing the weight of salt experimented upon this reduction could be prevented. It was found that even when a mixture of 1 centigrm. of cobalt chloride, and 40 centigrms. of borax were fused in the oxidising flame, some cobalt was reduced, though only a very minute quantity.

In the experiments with cobalt, the metallic bead always became very difficultly fusible ; and on solidifying it entirely lost its globular form, and flattened out in a very remarkable manner, sometimes even becoming branched. A similar flattening of the metal bead was observed in the case of chromium, and to some extent in that of aluminium.

No experiments were made on manganese in this series.

The number of experiments made with difficultly reducible oxides in this series was very large, but as the results obtained were of a negative character, we have not considered it necessary to give the details of the individual experiments.

(To be continued).

ANALYSIS OF SODIUM ALUMINATE.

By G. LUNGE.

A KNOWN quantity of the sample is dissolved in a given quantity of water, the proportion of residue insoluble in water being determined at the same time. A measured quantity of the solution is mixed with phenolphthalein, and titrated whilst hot with normal acid until the red colour disappears. The result shows the quantity of soda combined with alumina or silica. There is then added to the same liquid one drop of the solution of methyl orange, and it is titrated further. During this second titration the liquid is to be kept moderately warm, say 30°—37°. If necessary it is either cooled or set in a warm place. The titration is completed when the yellow colour of the liquid changes to a permanent red. As now all the alumina is converted into aluminium chloride or sulphate, the alumina present can be simply calculated from this titration. It is at once found in grms. by multiplying the difference of the two readings of the burette by 0·017 if normal acid has been used, or by 0·0017 in case of decinormal acid.

In technical determinations small quantities of silica, if present, may be neglected. It is more accurate to determine them and deduct their amount calculated as orthosilicate. The presence of large quantities of silica, however, excludes the use of the titration method.—*Zeit. Anal. Chemie*, vol. xxx., p. 471.

NOTICES OF BOOKS.

Examination of Water for Sanitary and Technical Purposes. By HENRY LEFFMANN, M.D., Ph.D., and W. BEAM, M.A. Second Edition, Revised and Enlarged, with Illustrations. Philadelphia : Blakiston, Son, and Co. London : Kegan Paul, Trench, Trübner, and Co. 8vo., pp. 130.

THIS work does not cover exactly the same ground as that by Professor Wanklyn, the eighth edition of which we had the pleasure of noticing a few weeks ago. As regards the strictly chemical examination of waters the two works run nearly parallel. Both give very similar instructions for the collection of samples, though Messrs. Leffmann and Beam use in place of the Winchester quart, commonly employed in Britain, the Penn " Demijohn,"—a kind of case bottle not known in this country. A useful hint is that " care should be taken to fill the vessel with as little agitation with air as possible." The instructions for the determination of total solids and chlorine call for no remark.

For the determination of nitrogen present as ammonia, and in organic compounds, the authors give the well-known Wanklyn process. To colorimeters they give the name " colour comparators." The Frankland and Armstrong method they consider liable to inaccuracies, but they describe and recommend the Kjeldahl process. The determination of the " oxygen consuming " power, as carried out by means of permanganate according to the instructions of Drs. Tidy and Dupré, is fully described, although the authors remark that such methods are limited in value.

Fleck's process (reduction effected by boiling the water with an alkaline solution of silver thiosulphate), they find open to the same objections as the permanganate process without any decided advantage.

They describe a process—the molybdic method—for the detection and determination of soluble phosphate, and they regard the presence of more than 0·6 part per million of PO_4 a suspicious feature, though its absence is no positive proof of freedom from organic pollution. Professor Wanklyn, on the other hand, attaches little importance to the presence of phosphates. Heisch's well-known sugar-test, according to F. E. Lott and Dr. Frankland, develops fungoid growths most decidedly in a water containing soluble phosphates. Our own experience convinces us that in any process for the treatment of sewage and other waste waters, the elimination of such phosphates is a necessary condition of success.

A method for the determination of free oxygen in water is given as proposed by Blarez. Among poisonous metals which may be present in waters the authors do not, like too many authorities, overlook chromium, which in manufacturing districts is far from uncommon. Boric acid, we think, will rarely be present.

For the spectroscopic examination of water, which may sometimes be useful, the authors use a small direct vision spectroscope. They also recommend in some cases a determination of specific gravity. But their method of procedure seems to us less satisfactory than that of Wanklyn, nor do they propose to use it, as he does, as a check on the total results of analysis.

The action of water upon lead is made the subject of a section. The following substances are specified as promoting the corrosion of lead piping : free acids and alkalies, oxygen, nitrates, especially those of potassium and ammonium, chlorides, and sulphates. On the other

hand, the following substances are characterised as non-corrosive and as preventing corrosion: calcium carbonates, acid sodium and ammonium, calcium silicate, silica, and soluble phosphates.

The degree of hardness has, in the opinion of the authors, little bearing on its sanitary value. This may be true as regards water ingested, though accurate comparative experiments are still wanting. But it cannot be accepted where the use of the waters for personal ablution is concerned. To wash in hard waters with the aid of soap is well known to coat the skin with a gluey film which cannot other than interfere with the free action of the pores.

Instructions for the biological examination of water are given at some length. The remark is made that "the presence of any of the higher orders of organic forms may be taken as an indication of moderate purity, as these are absent from very foul water." This rule cannot be absolutely accepted, since certain plants, *e.g.*, watercress, flourish better in undiluted sewage than in river water. But in industrial waste waters the higher animals and plants will certainly be absent. *Beggiatoa alba* indicates sulphur compounds rather than organic pollution. In concluding this chapter the authors admit that bacteriological studies, though often difficult to interpret, have yet been in certain cases of much value.

In speaking of the technical applications of water, magnesium chloride is justly pronounced very hurtful. The examination of a water for steam purposes should, it is said, include determination of free acid, total solids, SO_4, Cl, Ca, Mg, temporary and permanent hardness. No general rules are laid down for general manufacturing purposes, save that the nearest possible approach to chemical purity should be sought for. The dangers attending the presence of iron in the waters used in dye and bleach works are not overlooked.

The book before us may be safely recommended for the use of sanitary officials, analysts, and industrial analytical chemists as a useful addendum to their reference-works.

CORRESPONDENCE.

THE INSTITUTE OF CHEMISTRY AND ADVERTISING CERTIFICATES.

To the Editor of the Chemical News.

Sir,—The communication of Dr. Arthur P. Luff in your last number (Chem. News, vol. lxiv., p. 176) raises many important issues, which require consideration not merely from a purely ethical standpoint, but also with regard to the commercial interests of those parties who advertise analytical certificates.

That the Institute of Chemistry could and should pursue some course of action, besides existing, collecting fees, and issuing a periodical register, is the opinion of certainly a majority of its members. Just as Macaulay said there are in a Turkey carpet all the colours which, when properly arranged, will make a picture, so it may be said there are in the Institute of Chemistry all the elements necessary to the constitution of an ideal professional Institute; but there is, unfortunately, a considerable lack of arrangement. Perhaps when other chemical interests than those of the professorial class are more adequately represented on the governing body, a healthful desire to be more useful may be witnessed in that quarter. Whatever might be done, however, it would be of the greatest importance to take care that while a judicious control should certainly be exercisable, as Dr. Luff suggests, over palpably dishonest or professionally immoral conduct, there should be no undue interference with the liberty of the subject. Commercial men and firms have a perfect right to seek testimony to the value of their

products and processes from a particular or a general point of view; and they also have an an indefeasible right to use the testimony for which they pay. Of what earthly use is it to a manufacturer in these days to have a good article and to have it so certified unless he be allowed to publish such evidence?

There is a good deal of sentiment current amongst many medical men as to the publication of their views concerning things commercial; but perhaps this is only reasonable, since medical opinions are not, in the great majority of instances, based upon ascertained facts: they are sometimes built up upon a basis of experience, but cannot be put to any real test, or they are mere expressions of personal conviction not infrequently of a worthless character.

I do not desire for one moment to defend any really dishonest or otherwise blameworthy conduct of analytical and consulting chemists, but so long as their reports deal with matters of fact, and the inferences fairly deducible from them, they should be allowed full liberty of action.

Writing as a manufacturer and as a professional chemist, it seems to me that if manufacturers are not to be allowed to publish as they please proper reports for which they are willing to pay, they will certainly not engage the services of gentlemen who are so finikin concerning the discharge of one of the most important functions of their professional life, viz., certifying to the manufacturer and to the public alike, certain definite values of commodities, &c., offered for public sale or use; but the manufacturer will get the evidence he requires all the same, to the loss only of the said professional men.

I offer these remarks not so much by way of reply to Dr. Luff, whose views may or may not coincide with mine, but because I think if the subject is to be discussed it cannot be thrashed out too exhaustively.—I am, &c.,

C. T. Kingzett, F.I.C., F.C.S.

ESTIMATION OF NITRIC ACID.

To the Editor of the Chemical News.

Sir,—In nearly all works on Analysis, the method of estimating nitric acid by means of the "copper zinc couple" is given. I have tried the plan as given in Thorpe's "Quantitative Analysis," but always with a *perfectly negative* result. A pupil of mine who has made several attempts recently has arrived at the same result. Is there any special procedure to be adopted?

I have obtained very satisfactory results by the following process:—About half a grm. of KNO_3 is boiled with the "couple," an excess of oxalic acid being added. The boiling is continued for half an hour, then soda added, and the distillation carried on as usual for the estimation of ammonia.

I may mention that I have always succeeded by digesting a nitrate with the "couple" for some time in an acid solution and then "nesslerising" the solution.—I am, &c.,

W. A. Rudge.

Devon Lodge, Plymouth.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxiii., No. 12, September 21, 1891.

This issue contains no chemical matter.

Moniteur Scientifique, Quesneville.
Series 4, Vol. iv., Part 2, No. 587.

New Method for Preparing Chlorine.—P. de Wilde and A. Reychler.—The authors melt together hydrated magnesium sulphate, 246 parts; magnesium chloride, 203 parts; and manganese chloride, 198 parts. On evaporating away the water of crystallisation, hydrochloric acid escapes and there is obtained a greyish rose coloured residue, hard, brittle, and very hygroscopic, consisting of a mixture of manganese sulphate and chloride, and manganese chloride almost entirely free from water. If this matter is heated to dull redness in contact with air in a muffle, there escape simultaneously hydrochloric acid and chlorine, and there remains a black porous consistent residue, an intimate mixture of anhydrous magnesium sulphate and magnesium manganite, $Mg_3Mn_3O_8$. If this mixture is introduced into a porcelain tube heated to about 425°, there occurs a very regular escape of chlorine mixed with watery vapour, and, towards the end of the operation, a gradually increasing quantity of hydrochloric acid not utilised. One-fourth of the chlorine contained in the hydrochloric acid escapes in the shape of gaseous concentrated chlorine, and the remaining three-fourths are transformed into anhydrous magnesium and manganese chlorides. The tube is then raised to 525° and is traversed by a current of dry air, when there occurs a new escape of chlorine. The mixture of magnesium sulphate and magnesium manganite is then re-constituted and can again be submitted to the action of hydrochloric acid below nascent redness, which is anew followed by treatment with air at nascent redness, and so continuously. The authors allege that by their process the minimum yield is 70 per cent of the hydrochloric acid employed, whilst Weldon's process yields only 30 per cent. It appears that in France the price of hydrochloric acid (strength ?) has risen from 6 to 7 francs per 100 kilos.

New Method for the Volumetric Analysis of Sulphur Chloride.—G. A. Le Roy.—The author's method is based on the use of standard solutions. The chloride of sulphur is weighed into a tared phial and measured with a pipette of narrow calibre. The quantity is received into a dilute solution of pure soda (19·37 Na_2O per litre = 10 grms. sulphur per litre), of which a known volume has been taken. The chloride is decomposed, yielding sodium sulphide, thiosulphate, sulphite, sulphate, and chloride, and free sulphur separates out. It is heated, when the free sulphur quickly dissolves. When all the sulphur has disappeared, pure oxygenated water is added to the refrigerated liquid, which is then gently heated. The compounds of sulphur combined with soda are thus oxidised and converted into sodium sulphate. The excess of oxygenated water is then destroyed by heating the liquid to ebullition. The residual excess of soda is then titrated with a standard solution of pure nitric acid (39·35 NO_3H per litre), in presence of litmus or orange 3 as indicator. To this quantity of soda thus determined there is added the quantity of soda corresponding to the sodium contained in the sodium chloride formed by the action of the sulphur chloride, a quantity determined in the second part of the process (determination of chlorine). This total is deducted from the quantity of soda originally used; the difference represents the quantity of soda transformed into sodium sulphate, from which the sulphur is calculated. n c.c. of the solution of soda sulphated × 0·010 = N grms. of sulphur. In the liquid, neutralised, and thus freed from sulphides or thiosulphates, we determine the chlorine by a standard solution of silver in the known manner.

Vegetable Butter.—F. Jean.—An alimentary fat has for some time been manufactured at Mannheim from the oils of the kernel of the cocoanut (*Cocos nucifera*). A hectare of cocoa palms, representing 225 trees, yields yearly 800 kilos. of oil. Hitherto the use of these oils has been hindered by their acrid flavour; but by treatment with alcohol and animal charcoal the rancid flavour is removed, and the product is rendered white. This purified fat is now manufactured at Argenteuil and Amsterdam. It is the only fat which is analogous to cow butter, as it contains the same proportion of soluble fats. It has the advantage of being perfectly free from pathogenic organisms. (Could not this cocoanut butter be made more economically in India, Ceylon, &c., thus dispensing with the carriage of the useless parts of the nut ?)

Syntheses effected in the Group of the Sugars.—Emile Fischer.—A lecture delivered before the German Chemical Society.

On Bees'-Wax.—A. and P. Buisine.—The completion of a long illustrated paper.

On Bleaching - Chlorides. — MM. Osterberger and Capelle.—An exposure of certain alleged substitutes for bleaching-lime.

Preparation of certain Fluorides, and their Industrial Value.—Max Metto (*Zeit. Ang. Chemie*).—Process for obtaining artificial cryolites.

Process for Preparing Aluminium Hydroxide and the Alkaline Aluminates.—(*Dingler's Journal*).—The alkaline liquor resulting from the decomposition of the aluminate is concentrated by evaporation and then calcined directly with beauxite.

Presence of Vanadium in Caustic Potassa.—Edgar Smith.—From the CHEMICAL NEWS.

Preparation of Crystalline Iron Disulphide from Anhydrous Ferric Chloride and Phosphorus Pentasulphide.—E. Glatzel.—From the *Berichte d. Deut. Chem. Gesellschaft.*

Coefficient of the Utilisation of Gases. — C. W. Jurisch (*Chemische Industrie*).— A purely mathematical paper.

On Wool.—Dr. A. Horwitz (*Faerber Zeitung*),—This memoir seems founded on a lecture delivered by Prof. Watson Smith, F.C.S., before the Society of Dyers and Colourists. The author remarks that without its normal lustre wool has the appearance of cotton, and if the lustre exceeds a certain degree the wool is more transparent and does not take all colours equally well. Hence, if it is mixed with normal wool it may occasion uneven shades. In dyed wools, the hygroscopic property varies with the colour. The absorption of moisture decreases in the following series :—Black, blue, red, green, yellow, and white.

The Constituent Principles of Linen. — C. F. Cross and E. J. Bevan.—From the *Journal of the Chemical Society.*

Distinction of the Fibres of Jute, Linen, and Hemp.—W. Lenz.—Already noticed under *Zeitschrift Anal. Chemie.*

New Methods of Preparing Waterproof Cloth.—Em. Döring (*Romen's Journal*).—These methods may be divided into two groups. In some, a precipitate of salts of the fatty acids is produced upon the tissue itself; in others, the cloth is saturated with melted or dissolved substances, which, when they are once solidified on the fibre, have the property of repelling water. If any of the former class of methods is selected, the cloth is passed into a special machine in which it is saturated with aluminium acetate; it is dried and passed into a soap-beck. It is necessary in this operation to produce a basic compound. For this purpose, there are employed equal weights of salts of aluminium and of lead. Care must be taken not to introduce too large quantities of free acid with the aluminium sulphate, since the latter contains always a certain quantity of sulphuric acid, which, during desiccation, displaces the acetic acid. To avoid this inconvenience, there are added per litre from 10—80 grms. of soda. The most favourable temperature is 50°. Heating by direct steam must be avoided. For preparing the soap bath the author utilises the fact that an aqueous solution of soap forms true solutions with

mixtures of fat and wax, resins, mineral oils, and even caoutchouc. To this end, he takes a 10 per cent solution of gum paraguay in oil of turpentine. The proportions to be employed for a square metre of cloth are 30 grms. tallow soap, 25 Japan wax, 1·5 gum paraguay, 1 grm. good varnish. The wax is first melted, the gum and the varnish are added, and then for each kilo. of the solid gum there are added 0·5 grm. of a solution, saturated in heat, of potassium sulphide (liver of sulphur). The mixture is stirred and boiled, when sulphuretted hydrogen is liberated. A boiling solution of soap is added, when the bath is fit for use.

Sugars, Starches, and Gums.—Papers from the *Chemiker Zeitung, Liebig's Annalen*, the *American Chemical Journal*, and the *Zeit. Anal. Chemie.*

Identity of Cerebrose and Galactose.—H. Brown and Harris Morris.—From the *Journal of the Chemical Society.*

On Arabinose.—C. O'Sullivan.—From the *Journal of the Chemical Society.*

Detection of Nitrous Products in Sulphuric Acid. —H. Wilson.—From the *Pharmaceutical Journal.*

Determination of Nitrous Acid in Presence of Nitric Acid.— W. Kalmann.— From the *Zeit. Anal. Chemie.*

The Double Potassium and Mercury Iodide as a Reagent for Aldehyds.—L. Grismer (*Deutsch. Chemiker Zeitung.*—The aldehyds give with an alkaline solution of double potassium and mercury iodides a precipitate which varies from yellowish white to reddish brown or black, according to the dilution.

Detection of Traces of Copper in Distilled Water. —Herman Thoms (*Pharm. Central Halle*). — Distilled water, the purity of which has been ascertained by the ordinary methods, becomes coloured yellow on dissolving in it potassium iodide. A closer examination admits of the detection of infinitesimal quantities of copper, which neither ammonia nor potassium ferrocyanide had revealed. The presence of this impurity occasions the yellow colouration of the solution of potassium iodide in the water. The reagent gives a feeble yellow colouration with 1 part in 200,000 parts of water. The liquid must not contain any other substance capable of decomposing the iodide and liberating iodine.

MISCELLANEOUS.

Sulphuric Anhydride.—In the Chemical Section of the recent Congress of German Naturalists and Physicians, Prof. Dr. Rud. Weber exhibited a series of preparations from the Plettenberg Works in Westphalia, which are sent out in soldered tin boxes containing 2½ kilos. each. The anhydride was made according to Winkler's method, but no details were given. The speaker discussed the view as to the existence of two allotropic forms of sulphuric anhydride. According to his (Weber's) careful investigations, in which the anhydride was obtained absolutely free from moisture, by treatment with P_2O_5 and repeated distillation, it is in this state, at temperatures above 15°, a liquid which on cooling congeals to crystals resembling saltpetre, but which melt at the heat of the hand. Very small proportions of water cause this liquid to congeal at the heat of common temperatures, and the solid thus formed does not melt below 100°. It is a new compound, which in its empirical composition corresponds to the formula $4SO_3 + H_2O$. Sulphuric anhydride enters into direct combination with sulphur, selenium, and tellurium. With the former it yields a blue compound, insoluble in an excess of the anhydride, which Weber calls sulphur sesquioxide, S_2O_3. Selenium dissolves in the anhydride to a deep green compound, $SeSO_3$, and tellurium to a red liquid, $TeSO_3$.—*Chemiker Zeitung.*

THE CHEMICAL NEWS.

THE ORIGIN OF PETROLEUM.*

By O. C. D. ROSS, M.Inst.C.E.

PETROLEUM is one of the most widely distributed substances in Nature, but the question how it was originally produced has never yet been satisfactorily determined, and continues a problem for philosophers. In 1889 the total production exceeded 2,600,000,000 gallons, or about 10,000,000 tons, and, at fourpence per gallon, was worth about £44,000,000, while the recognition of its superior utility as an economical source of light, heat, and power, steadily increases; but, notwithstanding its importance in industry, the increasing abundance of the foreign supply, and the ever widening area of production, practical men in England continue to distrust its permanence; and owing to the mystery surrounding its origin, and the paucity of indications where and how to undertake the boring of wells, they hesitate to seek for it in this country, or even to extend the use of it whenever that would involve alterations of existing machinery. The object of this paper is to suggest an explanation of the mystery which seems calculated to dissipate that distrust, since it points to very abundant stores, both native and foreign, yet undiscovered, and even in some localities to daily renovated provisions of this remarkable oil.

The theories of its origin suggested by Reichenbach, Berthelot, Mendeleeff, Peckham, and others, made no attempt to account for the exceeding variety in its chemical composition, in its specific gravity, its boiling-points, &c., and are all founded on some hypothetical process which differs from any with which we are acquainted; but modern geologists are agreed that, as a rule, the records of the earth's history should be read in accordance with those laws of Nature which continue in force at the present day, e.g., the decomposition of fish and cetaceous animals could not now produce oil containing paraffin. Hence we can hardly believe it was possible thousands or millions of years ago, if it can be proved, that any of the processes of Nature with which we are familiar is calculated to produce it.

The chief characteristics of petroleum strata are enumerated as :—

    I. The existence of adjoining beds of limestone, gypsum, &c.
    II. The evidence of volcanic action in close proximity to them.
    III. The presence of salt water in the wells.

I. All writers have noticed the presence of limestone close to petroleum fields in the United States and Canada, in the Caucasus, in Burmah, &c., but they have been most impressed by its being " fossiliferous," or shell limestone, and have drawn the erroneous inference that the animal matter once contained in those shells originated petroleum; but no fish oil ever contained paraffin. On the other hand, the fossil shells are carbonate of lime, and, as such, capable of producing petroleum under conditions such as many limestone beds have been subjected to in all ages of the earth's history. All limestone rocks were formed under water, and are mainly composed of calcareous shells, corals, encrinites, and foraminifera—the latter similar to the foraminifera of " Atlantic ooze " and of English chalk beds. Everywhere, under the microscope, the original connection of limestone with organic matter—its organic parentage, so to speak, and cousinship with the animal and vegetable kingdoms—is conspicuous. When pure it contains 12 per cent of carbon.

Now petroleum consists largely of carbon, its average composition being 85 per cent of carbon and 15 per cent of hydrogen, and in the limestone rocks of the United Kingdom alone there is a far larger accumulation of carbon than in all the coal measures the world contains. A range of limestone rock 100 miles in length by 10 miles in width, and 1000 yards in depth would contain 743,000 million tons of carbon, or sufficient to provide carbon for 875,000 million tons of petroleum. Deposits of oil bearing shale have also limestone close at hand ; e.g., coral rag underlies Kimmeridge clay, as it also underlies the famous black-shale in Kentucky, which is extraordinarily rich in oil.

II. As evidence of volcanic action in close proximity to petroleum strata, the mud volcanoes at Baku and in Burmah are described, and a sulphur mine in Spain is mentioned (with which the writer is well acquainted), situated near an extinct volcano, where a perpetual gas-flame in a neighbouring chapel and other symptoms indicate that petroleum is not far off. While engaged in studying the geological conditions of this mine, the author observed that Dr. Christoff Bischoff records in his writings that he had produced sulphur in his own laboratory by passing hot volcanic gases through chalk, which, when expressed in a chemical formula, leads at once to the postulate that, in addition to sulphur, *ethylene* and all its homologues (C_nH_{2n}), which are the oils predominating at Baku, would be produced by treating—

  2, 3, 4, 5 equivs. of carbonate of lime (limestone) with
  2, 3, 4, 5   ,,   sulphurous acid (SO_2) and
  4, 6, 8, 10 ,,   sulphuretted hydrogen (H_2S) ;

and that marsh-gas and its homologues, which are the oils predominating in Pennsylvania, would be produced by treating—

  1, 2, 3, 4, 5 equivs. of carbonate of lime with
  1, 2, 3, 4, 5   ,,   sulphurous acid and
  3, 5, 7, 9, 11 ,,   sulphuretted hydrogen ;

Thus we find that—

Carbonate of lime, $2CaCO_3$, Sulphurous acid, $2SO_2$, and Sulphuretted hydrogen, $4H_2S$, } yield { $2(CaSO_4 . H_2O)$ (gypsum), $4S$ (sulphur), and C_2H_4, which is *ethylene*.

And that—

Carbonate of lime, $CaCO_3$, Sulphurous acid, SO_2, and Sulphuretted hydrogen, $3H_2S$, } yield { $CaSO_4.H_2O$ (gypsum), $3S$ (sulphur), and CH_4, which is marsh-gas.
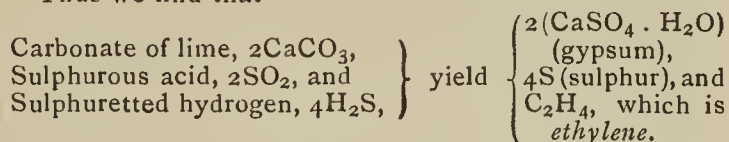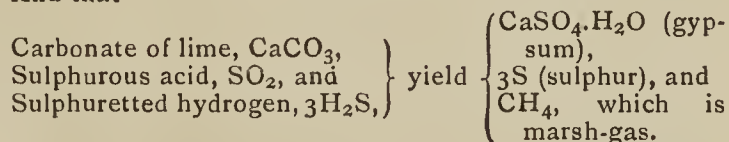
So that these and all their homologues, in fact petroleum in all its varieties, would be produced in Nature by the action of volcanic gases on limestone.

But much the most abundant of the volcanic gases appear at the surface as steam, and petroleum seems to have been more usually produced without sulphurous acid, and with part of the sulphuretted hydrogen (H_2S) replaced by H_2O (steam) or H_2O_2 (peroxide of hydrogen), which is the product that results from the combination of sulphuretted hydrogen and sulphurous acid—

$$(H_2S + SO_2 = H_2O_2 + 2S).$$

It is a powerful oxidising agent, and it converts sulphurous into sulphuric acid. Thus—

$CaCO_3$, H_2S, $2H_2O$, } yield { $CaSO_4.H_2O$ (gypsum) and CH_4, which is marsh-gas.

And—

$2CaCO_3$, $2H_2S$, $2H_2O_2$, } yield { $2CaSO_4.H_2O$ and C_2H_4, which is *ethylene*.
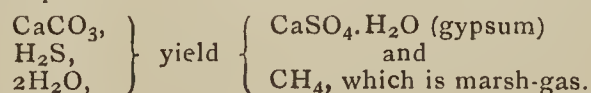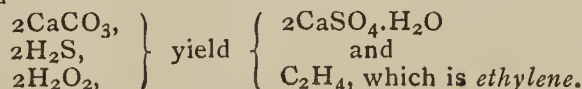
Tables are given at the end of the paper showing the formulæ for the homologues of ethylene and marsh-gas

Formulæ Showing how Ethylene and its Homologues (C_nH_{2n}) are Produced by the Action of the Volcanic Gases H_2S and H_2O_2 on Limestone.

Carbonate of lime.		Sulphuretted hydrogen.		Peroxide of hydrogen.		Gypsum.		Ethylene and its homologues.	Boiling-point.
$2CaCO_3$	+	$2H_2S$	+	$2H_2O_2$	yield	$2(CaSO_4.H_2O)$	+	C_2H_4 ethylene (gaseous).	
$3CaCO_3$	+	$3H_2S$	+	$3H_2O_2$	,,	$3(CaSO_4.H_2O)$	+	C_3H_6	
$4CaCO_3$	+	$4H_2S$	+	$4H_2O_2$	,,	$4(CaSO_4.H_2O)$	+	C_4H_8	
$5CaCO_3$	+	$5H_2S$	+	$5H_2O_2$	,,	$5(CaSO_4.H_2O)$	+	C_5H_{10}	
$6CaCO_3$	+	$6H_2S$	+	$6H_2O_2$	,,	$6(CaSO_4.H_2O)$	+	C_6H_{12}	
$7CaCO_3$	+	$7H_2S$	+	$7H_2O_2$	,,	$7(CaSO_4.H_2O)$	+	C_7H_{14}	—
$8CaCO_3$	+	$8H_2S$	+	$8H_2O_2$	,,	$8(CaSO_4.H_2O)$	+	C_8H_{16}	189° C.
$9CaCO_3$	+	$9H_2S$	+	$9H_2O_2$	,,	$9(CaSO_4.H_2O)$	+	C_9H_{18}	136° C.
$10CaCO_3$	+	$10H_2S$	+	$10H_2O_2$	,,	$10(CaSO_4.H_2O)$	+	$C_{10}H_{20}$	160° C.
$11CaCO_3$	+	$11H_2S$	+	$11H_2O_2$	,,	$11(CaSO_4.H_2O)$	+	$C_{11}H_{22}$	180° C.
$12CaCO_3$	+	$12H_2S$	+	$12H_2O_2$	,,	$12(CaSO_4.H_2O)$	+	$C_{12}H_{24}$	196° C.
$13CaCO_3$	+	$13H_2S$	+	$13H_2O_2$	,,	$13(CaSO_4.H_2O)$	+	$C_{13}H_{26}$	240° C.
$14CaCO_3$	+	$14H_2S$	+	$14H_2O_2$	,,	$14(CaSO_4.H_2O)$	+	$C_{14}H_{28}$	247° C.
$15CaCO_3$	+	$15H_2S$	+	$15H_2O_2$	,,	$15(CaSO_4.H_2O)$	+	$C_{15}H_{30}$	—

resulting from the increase in regular gradation of the same constituents.

It is explained that these effects must have occurred, not at periods of acute volcanic eruptions, but in conditions which may be, and have been observed at the present time, wherever there are active solfataras or mud volcanoes at work. Descriptions of the action of solfataras by the late Sir Richard Burton and by a British Consul in Iceland are quoted, and also a paragraph from Lyall's " Principles of Geology," in which he remarks of the mud volcanoes at Girgenti (Sicily) that *carburetted hydrogen* is discharged from them, sometimes with great violence, and that they are known to have been casting out water, mixed with mud and *bitumen*, with the same activity as now for the last fifteen centuries. Probably at all these solfataras, if the gases traverse limestone, fresh deposits of oil-bearing strata are accumulating, and the same volcanic action has been occurring during many successive geological periods and millions of years; so that it is difficult to conceive limits to the magnitude of the stores of petroleum which may be awaiting discovery in the subterranean depths.*

Gypsum may also be an indication of oil bearing strata for the substitution in limestone of sulphuric, for carbonic acid can only be accounted for by the action of these hot sulphurous gases. Gypsum is found extensively in the petroleum districts of the United States, and it underlies the rock-salt beds at Middlesboro', where, on being pierced, it has given passage to oil-gas, which issues abundantly, mixed with brine, from a great depth.

III. Besides the space occupied by " natural gas," which is very extensive, 17,000 million gallons of petroleum have been raised in America since 1860, and that quantity must have occupied more than 100,000,000 cubic yards, a space equal to a subterranean cavern 100 yards wide by 20 feet deep, and 82 miles in length, and it is suggested that beds of " porous sandstone " could hardly have contained so much; while vast receptacles may exist, carved by volcanic water out of former beds of rock salt adjoining the limestone, which would account for the brine that usually accompanies petroleum. It is further suggested that when no such vacant spaces were available, the hydrocarbon vapours would be absorbed into, and condensed in, contiguous clays and shales, and perhaps also in beds of coal, only partially consolidated at the time.

There is an extensive bituminous limestone formation in Persia, containing 20 per cent of bitumen, and the

* Professor J. Le Conte, when presiding recently at the International Geological Congress at Washington, mentioned that in the United States extensive lava floods have been observed covering areas from 10,000 to 100,000 square miles in extent, and from 2000 to 4000 feet deep. We have similar lava flows and ashes in the North of England, in Scotland, and in Ireland, varying from 3000 to 6000 feet in depth. In the Lake District they are nearly 12,000 feet deep. Solfataras are active during the intermediate, or so-called " dormant," periods which occur between acute volcanic eruptions

theory elaborated in the paper would account for bitumen and oil having been found in Canada and Tennessee embedded in limestone, which fact is cited by Mr. Peckham as favouring his belief that some petroleums are a " product of the decomposition of animal remains."

Above all, this theory accounts for the many varieties in the chemical composition of paraffin oils in accordance with ordinary operations of Nature during successive geological periods.

ON A COMBINATION OF WET AND DRY METHODS IN CHEMICAL ANALYSIS.*

PART I.

By W. E. ADENEY, F.I.C., Assoc.R.C.Sc.I., Curator, Royal University of Ireland; and T. A. SHEGOG, A.I.C., Assoc.R.C.Sc.I., Assist. Chemist, Royal College of Science, Dublin.

SECOND SERIES OF EXPERIMENTS.

ANOTHER series of experiments was now made differing from the preceding ones in this respect. In all cases the substance and fluxes were fused together in a shallow cavity in charcoal, the oxidising flame being employed, the beads on cooling were transferred to a cavity of the usual shape and size, metallic silver added in the form of a button, and the whole heated in the reducing flame.

Difficultly Reducible Metallic Oxides.

Three decigrms. of each substance, fused with twelve decigrms. of borax in the oxidising flame on charcoal, then nine decigrms. (in the case of cobalt, twelve decigrms.) of silver in the form of a button added, and the fusion continued, the reducing flame being employed.

Iron (Ferrous Sulphate).—The metallic bead became quite infusible, but fused when the flame was removed; a very faint trace of iron was found in the metallic bead.

Cobalt (Cobalt Chloride).—The metallic bead was difficultly fusible on cooling; it flattened out in the way already described for cobalt (see First Series of Experiments). It was found on testing to contain a small quantity of cobalt.

Aluminium (Aluminium Phosphate).—The metallic bead was somewhat infusible. Throughout the fusion a considerable quantity of metallic scale appeared on the glass bead. On testing the metallic bead, aluminium was found present.

Chromium (Chromium Nitrate).—The metallic bead was very difficultly fusible; on solidifying, it flattened out as already described for cobalt and chromium (see First Series of Experiments). On testing, a small quantity of chromium was found present.

Easily Reducible Metallic Oxides.

Metal.	Quantities of Fluxes and substance.	Deci-grms.	Reduction.	Remarks.
Antimony ..	Tartar emetic	3	Practically complete.	The fusion requires great care, and must be cooled in coal-gas. A very minute trace of antimony was found in the borax bead.
	Borax..	12		
	Silver..	9		
Tin	Stannic oxide	3	Incomplete.	The fusion went well, though the metallic bead was somewhat difficult to fuse. The assay was cooled in coal-gas. Although every care was taken, it was found impossible to entirely reduce the tin. The glass bead was quite transparent. An experiment was made, using the same quantities of stannic oxide and borax ; but, instead of silver, 12 decigrms. of metallic lead were added. This was unsuccessful, as the tin showed little tendency to alloy with the lead.
	Borax..	12		
	Silver..	9		
Lead	Lead acetate	3	Complete.	The fusion went very well, but was found to require great care. It was cooled in coal-gas. The borax bead was found to contain a trace of lead, but so small as to be inappreciable.
	Borax..	12		
	Silver..	12		
Arsenic . ..	Arsenic trioxide ..	3	Complete.	Volatilisation of arsenic occurred at the beginning of the fusion, but soon ceased. The fusion went easily, and a perfectly transparent glass bead was obtained. The assay was cooled in coal-gas. The glass bead was found to contain a scarcely detectable quantity of arsenic.
	Borax..	12		
	Silver..	9		
Silver	Borax..	12		The silver remained easily fusible.
	Silver..	9		
Bismuth ..	Bismuth nitrate crystals..	3	Incomplete.	The fusion went very satisfactorily. It was cooled in coal-gas. A small quantity of bismuth was found on testing the glass bead.
	Borax..	12		
	Silver..	12		
Copper.. ..	Copper sulphate (anhydrous)	3	Complete.	The fusion requires care. The borax bead was of a pale bottle green colour (proved to be due to iron). On testing the glass bead with sulphuretted hydrogen a very slight colouration was observed.
	Borax..	12		
	Silver..	9		
Nickel, No. 1	Nickel chloride . ..	3	Practically complete.	The fusion went fairly well, no fumes of arsenic were seen, and its volatilisation could only be detected by the garlic odour observed. The metallic bead was somewhat infusible, remaining all the time in a viscous state. The glass bead was tested for arsenic and nickel, and a mere trace of each was found present.
	Borax..	12		
	Sodium arsenate ..	2		
	Silver..	4		
		Centi-grms.		
No. 2	Nickel chloride . ..	5	Practically complete.	The fusion went well, both beads were easily fusible. The borax bead contained a mere trace of nickel.
	Borax..	25		
	Silver..	33		

NOTE.—No experiments were made with zinc in this series.

Manganese (Manganous Sulphate).—The metallic bead was at first infusible, but became more fusible towards the end of the experiment. A good deal of metallic scale appeared floating on the glass bead, even before the silver was added. On testing the metallic bead, manganese was found present.

It now only remains for us to make a brief reference to what has been done towards the solution of the third of the questions we wished to settle, namely, whether or not, when complex substances are fused with borax and sodium carbonate in the manner described, the constituent metals behave as in simple compounds.

In Dr. Davoren's estimations of nickel and cobalt by this method, no difficulty was experienced in effecting a complete separation ; the nickel was entirely reduced, and all the cobalt was found in the glass bead. From this it was thought that the presence of an easily reducible oxide might entirely prevent the reduction of a difficultly reducible oxide. It seemed probable that if this were found to be the case with bodies so allied in chemical properties as nickel and cobalt, it would in all probability be true of the other oxides ; experiments were therefore made with salts of these metals.

The salts were mixed with borax, and fused in the oxidising flame ; no silver was used. The side of the glass bead which had cooled in contact with the charcoal was invariably found covered with a layer of reduced metal. When the proportions of nickel to cobalt in the mixture was greater than 1 to 1, the reduced metal was entirely nickel. When, however, the cobalt preponderated in the mixture, a small quantity was always reduced with the nickel.

It will be seen that a considerable number of experiments are yet required, more especially to ascertain the behaviour of complex substances when treated in the way suggested by us ; and it was our original intention to complete the necessary experiments before publishing any results of our investigation. In the midst of our work, however, one of us, having been elected to the office of Curator in the Royal University, had to resign his position in the Royal College of Science. We have since found it impossible to continue the work jointly, and we have therefore thought it advisable to publish an account of the work which has been already done.

The investigation will be carried on by one of us.

A NEW GLASS SYPHONING EXTRACTION APPARATUS.*

By J. T. WILLARD and G. H. FAILYER.

BEFORE describing our apparatus, a few words in justification of its invention, notwithstanding the many forms already proposed, may not be out of place. First, we are led to reject any extractor which makes cork connections. The extreme difficulty of completely freeing cork from its resinous constituents can be appreciated only by one who has extracted the properly perforated corks for one hundred hours or more in a large Soxhlet's extractor, and at the end of that time has still found appreciable quantities of extract. Then, too, the more perfectly a cork is exhausted, the less suited does it become, mechanically, for use, losing its toughness and elasticity. Second, a *syphoning* apparatus must be preferable to a percolating, because we are certain that every particle of the substance is soaked by fresh solvent every time the container is filled, while in a percolating apparatus we can never be quite sure that the solvent is not chiefly flowing down channels of least resistance and leaving portions of the material comparatively unacted upon. Soxhlet's extractor, when made with ground joints will doubtless give good satisfaction. The form we are about to describe has, however, the advantage of greater simplicity, and is consequently cheaper and less liable to fracture.

By reference to the cut it will be seen that our extractor consists of four parts, viz., the *flask*, A; the *containing tube*, B; the *condensing tube*, D; and the *syphon*, C. The flask is small, holding about 100 c.c., and weighing about 20 grms. The containing tube is ground into the neck of the flask, and has a pocket on one side, in which the substance, enclosed in a sack formed of fat-free filter-paper, is placed for extraction, and into which the short arm of the syphon dips. The condensing tube expands to a stopper for the containing tube, and at the lower end is drawn out and ground off in such a way as to direct the condensed solvent into the pocket containing the substance for analysis. The upper part of the condensing tube passes through a cold water jacket of some kind; ours is a copper tank large enough for six extractors. The syphon is made of small tubing, the inside diameter being about 2 m.m. At the bend it must be less, but must not be constricted so much as to greatly impede the flow of the liquid through. The capillary attraction exercised by the inner wall of the syphon raises the liquid sufficiently to bring the syphon into action before the pocket is full enough to run over. The upper end of the short limb of the syphon must not be too close to the side of the pocket or the capillary action of the outside of the syphon, and the side of the pocket will draw the liquid over without filling the syphon. To prevent this, the syphon may be bent sharply away from the wall of the pocket, as shown in the cut, or the wall itself may bend away at that point. If these details be met in the construction of the syphon, it will empty the pocket promptly, and the apparatus will require no attention after the flame is adjusted under the water-bath.

The apparatus is so constructed that the syphon may be easily removed, and when the extraction is concluded the substance and the syphon are removed, and the solvent distilled up into the pocket. If too large an excess has not been taken, the removal of the syphon and the substance will give ample capacity to the pocket to

receive the solvent remaining. The drying of the extract is completed in hydrogen as usual.

The extractor, as figured, was constructed for the quantitative analysis of feeding stuffs. The containing pocket was therefore made small to insure quick syphoning and to require but little absolute ether. It is, however, apparent that within certain limits the apparatus might be made of considerable size. We have more recently had a number constructed, especially for milk analysis. In these the containing pocket is made large enough to admit the paper coil upon which the milk is dried if Adams's method is employed, or a drying tube filled with asbestos when desiccation is effected upon that substance. These extractors are each provided with two flasks, thus doubling their efficiency and enabling one to keep them all in constant service.

Our extractors are so arranged that each set of six is heated by a single water-bath. This consists of a flat copper box. The extractors are held up in place by strong spiral brass springs. Each spring has a piece of brass gauze soldered across the upper coil. The diameter of the coil is greater than that of the bottom of the flask. The springs, while rather stiff, must be so adjusted in length as to require but little compression to bring them in position.

We have used the extraction apparatus above described in the analysis of feeding stuffs for over a year and a half with the greatest satisfaction. Fitted with two flasks, and charged with absolute ether, which is protected by a calcium chloride tube in the upper end of the condensing tube, the apparatus seems to us to leave little to be desired in simplicity or perfection of action.

NOTE.—Mr. J. T. Crawley, in the *Am. Chem. Journ.*, vol. xi., p. 507, has described an apparatus employing capillary attraction to bring the syphon into action. It seems right to say that our extractor was designed before the publication of his article.

THE DIRECT DETERMINATION OF ALUMINIUM IN IRON AND STEEL.*

By THOMAS M. DROWN and ALEX. G. McKENNA,
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THE unsatisfactory character of most, if not all, of the processes for the direct determination of alumina in the presence of iron and phosphoric acid, and the sharpness with which both the iron and phosphoric acid can be determined, have led chemists to rely mainly on processes in which the alumina is obtained by difference. But in the modern alloys of aluminium and iron, where the aluminium may be present only to the extent of a small fraction of 1 per cent, nothing short of the isolation of the alumina itself can give satisfactory evidence of its presence.

In the course of some experiments on the electrolytic deposition of metals, we have found that it is possible to remove iron completely from its acid solution in large quantity and in short time, by a current that will not in the least affect the alumina in solution. The essential condition of success in this operation is the use of mercury as a cathode, the iron forming an amalgam with mercury as fast as it is deposited from solution. This use of mercury was proposed by Dr. Wolcott Gibbs, in a paper read before the National Academy of Science in 1883, as a method of determining many metals by electrolysis which are not at all, or only imperfectly, deposited on a platinum cathode. It is certainly one of the most valuable and suggestive contributions to the quantitative separation and determination of metals by electrolysis that has yet been made.

The following are some of the experiments we have made to determine the conditions of success in the application of the method to the determination of aluminium in the presence of iron.

First, as to the completeness of the precipitation of the iron. The first attempts to determine the iron which had been removed from the solution and alloyed with the mercury showed an apparent loss, notwithstanding the fact that the iron was completely removed from solution. This was subsequently found to be due to the volatilisation of some of the mercury on drying before weighing. The amount of mercury which may be thus lost is very considerable, as the following experiments show.

About 75 grms. of mercury were put into a beaker, which was then weighed. It was washed several times with water, and once or twice with alcohol. The loss on drying different times and at different temperatures was as follows:—

Time of drying.	Temperature.	Loss, Grm.
10 minutes.	140° C.	0·0096
,,	100°	0·0043
,,	,,	0·0028
,,	,,	0·0030
,,	,,	0·0030
,,	,,	0·0025
2 hours.	70°	0·0040
5 ,,	,,	0·0120
20 ,,	,,	0·0520
48 ,,	25°	0·0030
48 ,,	24°	0·0025
24 ,,	,,	0·0007
24 ,,	,,	0·0012
48 ,,	,,	0·0042
48 ,,	,,	0·0033

But it is, in fact, only necessary to heat the mercury for about two minutes at a temperature of 100° C. to free it completely from moisture, and in this time the loss is very small. The following are the amounts lost in nine experiments under these conditions:—0·0002, 0·0005, 0·0005, 0·0003, 0·0008, 0·0005, 0·0002, 0, 0, an average of 0·00033 grm.

There seems also, at times, to be a loss not connected with the volatilisation of the mercury, which, possibly, may be due to impurities in the mercury—metals, for instance,—which are dissolved out by the acid, and not precipitated on the mercury again. On this account it is desirable, in cases where the process is used to determine iron or other metal, to have a blank beaker in the circuit, containing only the mercury and dilute sulphuric acid, and to add any loss which may be found in this beaker to the amount found in the others in the series.

The following are a series of results obtained by electrolysing a solution of ferrous ammonium sulphate, slightly acidulated with sulphuric acid.

Iron taken. Grm.	Iron found. Grm.	Loss of weight in blank. Grm.	Iron found + loss in blank. Grm.
0·2260	0·2254	Not made	
0·3727	0·3725	,,	
0·3080	0·3089	,,	
0·3238	0·3232	,,	
0·0647	0·0632	0·0020	0·0652
0·0647	0·0634	Not made	
0·0647	0·0649	0·0000	0·0649
0·0647	0·0635	Not made	
0·0604	0·0602	0·0003	0·0605
0·0604	0·0608	0·0003	0·0611
0·3020	0·3008	0·0003	0·3011
0·3020	0·3000	0·0003	0·3003

The best conditions for the rapid precipitation of the iron are a strong current (about 2 amperes, or 20 c.c. of electrolytic gas a minute), a nearly neutral solution of small bulk, a large amount of mercury (not less than fifty times the weight of the iron to be precipitated), and a large anode of platinum. The mercury cathode is brought into the circuit by means of a platinum wire enclosed and fused into one end of a glass tube, which passes through the liquid. It is of advantage to pour mercury into this tube to the depth of an inch, in order to weight it and make the connection with the mercury cathode more stable.

By observing the above conditions it was found practicable to precipitate 10 grms. of iron in from 10—15 hrs. The iron amalgam may contain as high as 10 per cent of iron. On standing a long time exposed to the air, the iron separates out as a black powder, which may be removed from the mercury by agitation with water. Mercury which has been used for iron precipitations may be purified by removing the greater part of the iron amalgam by filtration through chamois skin, and then passing air through the filtered portion, as recommended by J. M. Crafts.

Second, as to the behaviour of manganese in solution under the foregoing conditions. Inasmuch as manganese is almost always present in iron and steel, a good many experiments were made to find what becomes of it under the electrolytic conditions which we have been considering. It was found that a portion is oxidised to the dioxide, coating the platinum anode, and ultimately falling off, in great part in scales, and that a portion is reduced to the metallic state and alloys with the mercury. This fact of the reduction of the manganese was evident on electrolysing a solution containing only dilute sulphuric acid, using as a cathode mercury which had been previously used in an experiment with a manganese solution. In a few minutes the permanganate colour appeared, and a slight coating of manganese dioxide was deposited on the anode. The experiments made to determine what proportion of manganese was reduced and what proportion oxidised were not satisfactory, but in general it may be said that about half the manganese alloys with the mercury; the other half is nearly all oxidised and is found both on the anode and in scales floating in the liquid. A small portion is always found in solution. By using both electrodes of platinum it was found possible, in the absence of iron, to precipitate manganese completely as dioxide; but the coating on the anode was never coherent when more than mere traces of manganese was present. But the danger of the re-solution of the floating particles of the manganese dioxide, together with the necessity of filtering and igniting it to the proto-sesquioxide, makes the process an unsatisfactory one for the determination of manganese. The best conditions were found to be a concentrated solution of manganese sulphate to which a little nitric acid had been added, a rather weak current, a small cathode, and a large anode.

Third, as to the influence of phosphoric acid on the precipitation of iron. Two solutions containing equal amounts of iron were electrolysed in series. To one was added 1 grm. of crystallised hydrogen di sodium phosphate, and to the other dilute sulphuric acid. When the iron was all precipitated, the beakers with the mercury, together with the glass tubes containing the platinum wires, were weighed, and found to have gained, respectively, 0·1290 and 0·1275 grm. To a solution of 3 grms. of iron in sulphuric acid, 0·1935 grm. crystallised hydrogen di-sodium phosphate was added, equivalent to 0·0167 phosphorus. After the iron was completely removed from the solution, the phosphoric acid was precipitated by magnesium mixture and 0·0163 grm. phosphorus obtained. A duplicate experiment gave 0·0161 grm. phosphorus. A third experiment with the same amount of iron gave, under like conditions, 0·0064 grm. phosphorus when 0·0068 was added. From the experiments we may conclude that the separation, by this electrolytic method, of iron and phosphoric acid in solution is satisfactory.

Fourth, as to the separation of iron and aluminium. Known amounts of iron and aluminium in solution to-

gether as sulphates were electrolysed, and, after all the iron had been deposited, the alumina was precipitated by ammonia. Following are two results thus obtained :—

Alumina taken. Grm.	Alumina found. Grm.	Iron taken. Grm.	Iron found. Grm.
0·0283	0·0286	0·2286	0·2277
0·0142	0·0142	0·2286	0·2283

The iron, determined by weighing the mercury after electrolysing the solution, includes in both cases a blank of 0·0020 grm., which was the loss of a mercury cathode in the same series, when dilute sulphuric acid only was electrolysed.

The process was now tried under the conditions which would obtain in the determination of aluminium in iron and steel, namely, known amounts of aluminium sulphate were added to a known amount of steel. After much experimenting the following procedure was adopted as being the most uniformly satisfactory.

Dissolve 5—10 grms. of iron or steel in sulphuric acid, evaporate until white fumes of sulphuric anhydride begin to come off, add water, heat until all the iron is in solution, filter off the silica and carbon, and wash with water acidulated with sulphuric acid. Make the filtrate nearly neutral with ammonia, and add to the beaker in which the electrolysis is to be made about one hundred times as much mercury as the weight of iron or steel taken. The bulk of the solution should be from 300—500 c.c. Connect with the battery or dynamo current in such a way that about 2 amperes may pass through the solution over night. This we have generally accomplished by using three lamps of 32-candle power arranged in parallel on an Edison circuit. In the morning the solution is tested for iron, and, if necessary, the electrolysis is continued after adding enough ammonia to neutralise the acid that has been set free by the deposition of the iron. The progress of the operation may be observed by the changing colour of the solution. At first it becomes darker in colour near the anode ; after five or six hours it is nearly colourless, and finally becomes pink, from the formation of permanganate.

When the solution gives no test for iron, it is removed from the beaker with a pipette while the current is still passing. When as much has been removed as possible without breaking the current, water is added, and the operation continued until the acid has been so far diluted that there is no danger of dissolving iron from the mercury. The anode is now taken out and the mercury washed with water until the last traces of the solution have been removed from it. After filtering, to remove any flakes of manganese dioxide which may be suspended in the solution, sodium phosphate is added in excess and ten grms. of sodium acetate. The solution is now made nearly neutral with ammonia and boiled for not less than forty minutes. The precipitate of aluminium phosphate is then filtered off, ignited, and weighed. It should be white after ignition. If it has more than the faintest shade of colour it must be dissolved by fusing with acid potassium sulphate, and again electrolysed for two or three hours. The second precipitate has been found to be always white without a trace of iron, but in general we have found the first precipitate to be free from iron or to contain such a minute amount that the second treatment is not necessary. We have determined that 0·0003 grm. of iron will give a decided red colour to 0·0076 grm. of aluminium phosphate. The precipitate of aluminium phosphate, produced as above, does not always have the composition Al_2O_3, P_2O_5. Our analyses of it go to show that the formula $7Al_2O_3, 6P_2O_5$ more nearly expresses its average composition, and in those cases in which the amount of phosphoric acid and alumina have not been actually determined in the precipitate, we have assumed this composition, which is equivalent to 24·14 per cent of aluminium in the precipitate.

It is necessary to boil for at least forty minutes to precipitate completely the aluminium phosphate, and excessive washing of the precipitate should be avoided.

The following table gives the result obtained in determining by the above process the aluminium added in known amounts to solutions of steel :—

Steel taken. Grms.	Percentage of aluminium added.	Percentage of aluminium found.
5	0·39	0·36
5	0·39	0·38
5	0·39	0·38
5	0·39	0·38
5	0·39	0·37
5	0·043	0·045
5	0·043	0·041
5	0·043	0·049
5	0·043	0·048
10	0·027	0·015
10	0·200	0·160
10	0·046	0·044
5	0·085	0·088

A blank experiment with the same steel, without the addition of any aluminium, gave a precipitate of aluminium phosphate equivalent to 0·004 per cent of aluminium, which has been deducted from the results in the above determinations. This small amount came, doubtless, from the reagents and the glass vessels used, and may have been partly silica. This correction should be made in all cases where the amount of aluminium is very small.

A sample of Mitis steel analysed by this method gave the following result :—

Steel taken. Grms.	Aluminium found. Per cent.
4·4260	0·014
4·4260	0·013
12 6650	0·014

A sample of "aluminium physic" used in the preparation of Mitis castings gave as follows :—

Iron taken. Grms.	Aluminium found. Per cent.
1·6130	6·28
0·4030	6·52
0·4030	6·22

A sample of pig-iron to which aluminium had been added in re-melting gave as follows :—

Iron taken. Grms.	Aluminium. Per cent.
1·4576	0·789
1·8167	0·806
1·6390	0·794
1·6130	0·802

It might be thought that the process would be simplified by reducing the iron to the state of protoxide, and then precipitating the alumina as basic acetate, subsequently removing by electrolysis the small amount of iron precipitated with the alumina. A number of experiments proved, however, that this modification not only gave less accurate results, but involved much more work than the precipitation of all the iron by electrolysis. When the iron is all removed over night without involving any work on the part of the analyst, it is surely superfluous to go through a more or less tedious chemical operation to remove a part of the iron.

It is obvious that this process of electrolysis with a mercury cathode may be of value in other analytical operations in which the removal of the iron would be of advantage ; as, for instance, in the determination of phosphoric acid by magnesia.

THE CARBAZOL METHOD FOR NITRATES IN WATER ANALYSIS.

By W. P. MASON.

So far as I am aware, no note is on record calling attention to the influence of temperature upon the results obtained by this method. Experimenting with solutions of potassium nitrate, containing 3·5 parts nitrogen per million of water, chilled to various temperatures, it was found that the cold solutions darkened much more slowly than the warmer ones. When the chilling was carried some degrees below zero the green colouration appeared very gradually indeed. It follows from this that the same precaution must be taken as when "nesslerising" for ammonia, namely, the standards and the solutions of unknown strength must be operated upon at the same temperature. It appears to be immaterial whether the tubes be cooled immediately, upon addition of the strong sulphuric acid, or be permitted to cool gradually before the carbazol solution is added. As has been already stated by Hooker, the carbazol solution was found to act better after its original yellow colour had passed into an olive-green; and, if kept in a stoppered flask, remained in good condition for use for forty-eight hours.

After very careful examination as to delicacy and uniformity of results, I must confess to some disappointment in the method.

Rensselaer Polytechnic Institute,
    Troy, N.Y., Oct. 1, 1891.

NOTE ON THE
INFLUENCE OF LIGHT UPON EXPLOSIVE GASES AND UNSTABLE COMPOUNDS.

By H. N. WARREN, Research Analyst.

THE apparatus employed in these experiments consisted of a powerful 15-inch lens, the light being supplied both by the lime burner and also by the combustion of magnesium. When a mixture of hydrogen and chlorine was brought under the influence of the former, combination took place, with explosion after a few minutes' interval; but when a ray of the latter was used almost instantaneous explosion followed. Rays of light of different colours were employed, consisting of red, green, and yellow; in each case the explosion was considerably retarded. In the case where a bright red beam was allowed to impinge, combination took place very slowly, amounting to the faintest explosion only.

Small quantities of chloride of nitrogen, as also iodide of that element and auric fulminate, were similarly treated, providing almost identical results.

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SCIENCE IN OUR MEDICAL SCHOOLS.

THE Introductory Addresses delivered at the re-opening of the London Medical Schools contain some utterances which, to those who long for a reform in higher education, appear not unpromising. Sir G. M. Humphry, F.R.S., is reported (*Medical Press*) to have said:—"I well remember the new life of joy that opened upon me when, at the age of sixteen, I passed from the drudgery of Latin and Greek and the other ordinary school subjects, to the study of the elementary facts and theories of physics and chemistry, and felt the glowing light of natural science dawn upon me, and realised the glorious liberty of walking in that light." He continues, speaking of the love of knowledge, "No human being is without that love; it is the heritage of everyone, and, damped though

it be by school routine and examination dread, it cannot be quite killed. . . . . The food which it requires, and upon which it flourishes best, is *fresh* knowledge." By "fresh knowledge" the speaker can only mean research, investigation as contrasted to the mere getting up what others have learnt already.

Yet again, the speaker declared "that which raised Newton, Darwin, and Hunter above the level of ordinary men, and made each so great a force in advancing science and thought, was the combination in each of unusual thinking or reasoning powers with that of careful observation." How sad, then, that our ordinary college curricula do so little to develop these powers.

As to the importance of scientific training for the many outside the professional classes, Prof. Victor Horsley, F.R.S., said at University College:—"The fact is that numbers of the public, especially of the highest and lowest classes, who for different reasons are the farthest removed from Science, are easily deceived by such abominations as the Mattei treatment, the faith-cure (there is also a scare-cure), and electropathic belts."

From such delusions only the scientific spirit can set us free, and hence we need not be surprised that quacks of all grades and kinds—of whom the quack medical is merely a single type—dread the cultivation of Science. Literary culture they do not dread. In fact, men of the highest standing in the "humanities" imbibe and propagate reigning delusions.

But not all the speakers at these re-openings seem to have felt the paramount importance of Science. Mr. H. Juler, F.R.C.S., is reported to have said, at St. Mary's Hospital, that to the embryo physician "previous education and training, *especially* in classics, mathematics, English, French, and German were of great assistance; but, *in addition* to these, a good practical knowledge of biology, chemistry, and physics were most essential." The *italics* are our own. Here it seems that the speaker gives a first place to words, and to the knowledge of things a mere additional rank.

In thus glancing over the medical papers we have met with a few painful facts. We learn with regret that the "Anti-vivisection" epidemic, which we had hoped was extinct, has attacked an eminent divine in a violent form. We are not a medical nor a biological organ, but, on the principle "*Jam proximus ardet Ucalegon*," we cannot view this recrudescence of a moral malady with indifference. Who knows whether some hysterical conscience will not suddenly denounce research in chemistry and physics?

THE SELF-PURIFICATION OF RIVERS.

IN the sanitary section of the German Congress of Naturalists and Physicians, Prof. von Pettenkofer read an important paper on this subject. His more immediate purpose was to inquire whether the sewage of Munich could be safely allowed to flow without treatment into the river Isar. A water is said to be polluted when it is no longer clear and inodorous, when fishes and plants perish in it, and when it contains more organic matter and less oxygen than are to be found in the unpolluted portions of its flow. Such contamination is essentially different from the transient turbidity due to heavy rains or to melting snow. Still, even the permanent pollutions disappear in the further course of the river bed, not merely by deposition, but by other agencies to be discussed below. Here the rapidity of the stream and the quantity of the water exert, as it is well known, a preponderating effect.

The most formidable impurities are considered to be the putrescent refuse which flows out of the sewers, and which very quickly produces an offensive odour at the places where they accumulate. In this respect very peculiar prepossessions have been developed; human

excretions are regarded as more dangerous than those of the lower animals; the overflow of cesspools is pronounced less objectionable than the discharge from water closets, and urine is declared less formidable than solid excrement. But the accurate researches of Von Voit have shown that an adult well-fed human being voids in 24 hours 1254 grms. urine, and only 31 grms. solid excreta. These figures are considerably reduced by the circumstance that the excretions contain not less than 92 per cent of water.

On evaporation the urine leaves only 65 grms. solid matter, including 20 grms. ash, and the excrement only 34 grms. containing 6 grms. ash. If we deduct the mineral matter, consisting of sodium chloride, alkaline chlorides, and earthy alkalies, which are perfectly harmless, the daily contaminations of the river amount only to 73 grms. per head. It is decidedly more difficult to estimate the impurities which the sewage contains in the form of commercial and industrial refuse, which play a very important part. According to the Saxon Board of Health (*Landes Medicinal Verwaltung*), the river-pollution due to industrial refuse is 93 per cent, as against only 7 per cent arising from sewage properly so-called.

Von Pettenkofer has for many years given his attention to this question, and has continually had researches conducted by his pupils. But nothing has hitherto altered the opinion which he expressed long ago that sewage may without hesitation be permitted to flow into a river, if its volume is not more than 1-15th that of the river water, and its rate of flow decidedly greater than that of the current. Nevertheless, most German local authorities prohibit in every case the introduction of crude sewage into a river. The speaker has encountered no little hostility, as he gave an opinion opposed to this practice for the waste waters of the city of Munich. To come to a decision on this question we must take the circumstances of the case into exact consideration.

Munich counts at present 280,000 inhabitants, who, if we set out from the figures of Von Voit as above cited, and overlook the fact that women, children, and the aged excrete less matter than adult and properly fed men, void daily 20,440 kilos. of putrescent organic matter, which in the course of a year gives the mighty total of 7,458,000 kilos.

If we start in the first moment at these figures the picture changes as soon as we take into account the volume of water flowing in the Isar. According to accurate observations this river discharges 40 cubic metres of water per second, or daily 3,456,000 cubic metres. If the quantity of pollution is weighed against this figure the former is only $\frac{6}{1000000}$, or 6 m.grms. per litre. This pollution is so inconsiderable that it cannot be detected by the eye if a corresponding mixture is made up experimentally. But it is also not permanent, for at Ismaning, 7 kilos. below Munich, the sewage influx is no longer to be detected, although now more than half the closets have been connected with the sewers. Still less is a detection of sewage matters to be detected bacteriologically or chemically at Freising, 33 kilos. below Munich. On January 21st of this year, samples of water were drawn from the Isar, both above Munich and at Freising. The former contained per litre 243 m.grms. solid residue, the second 252. The former required for oxidation 1·4 m.grm. oxygen and the latter 1·6. These differences are so small that they fall within the limits of experimental error. In this summer specimens were drawn on June 18th, July 22nd, and August 2nd, which gave on evaporation a mean residue of 197 m.grms. per litre, and required for oxidation 2·3 m.grms. oxygen. The circumstance that in winter the organic matter is one-half lower, and the inorganic matter higher than in summer, is explained by the affluents which feed the Isar. The melting snows and the heavy rains increase the organic matter in a manner easy to be understood.

The bacteriological researches conducted by Prausnitz equally prove the purifying power of the Isar. The number of 198,000 bacteria per c.c. found at the mouth of the Munich sewer was reduced at Ismaning to 15,231, and at Freising to 3602. These results agree with those of other investigators. Fränkel found in the water of the Spree above and below Berlin 6000 bacteria per c.c., but in the city a million. The mere number of bacteria found has, however, no sanitary significance, since the bacteria found in the water are almost exclusively harmless, and, indeed, destroy the pathogenic microbia in the struggle for existence. In fact, if we except the apparently untrustworthy statements of some French investigators, pathogenous bacteria have hitherto never yet been found in river water.

If they were present and, in spite of the enormous dilution, were able to produce infectious diseases, this would have become manifest by statistical facts. It might have been assumed formerly, when Munich was a notorious nest of typhus fever, that this was the cause of the cases of typhus in the towns situated lower down the Isar. But Munich has been almost freed from typhus by sanitary improvements, whilst the above-mentioned smaller towns in the Isar valley which have not amended their hygienic arrangements are still as abundant in typhus cases as they were in times when it was attempted to blame Munich for the infection.

If the self-purifying power of the Isar is thus demonstrated the question arises how it is effected. This has been repeatedly ascribed to subsidence, but nothing save Isar gravel has ever been found by dredging below Munich. As little has the author obtained any kind of deposit by allowing sewage to trickle continuously over a moving channel filled with gravel.

Von Pettenkofer ascribes the purifying action of rivers solely to the oxygen dissolved in the water in a free state or separated from organisms. In the latter respect the green algæ and other chlorophyllic or even non-chlorophyllic plants come prominently into consideration. It is therefore urgently requisite to preserve this vegetation, which may be destroyed by a too great concentration of the water to be purified, just as a field may be damaged by over-manuring. To this end the oxygen in the water, which is absorbed by the plants and given off again, must be present in sufficient quantity. On the other hand, industrial waste waters which destroy aquatic vegetation must not find entrance into the river unless previously purified. What part is played by oxygen may be observed in aquaria, where the sea water does not need to be renewed for months if air is passed through. The water remains clear, although it receives the excretions of the animals present and many residues of their food. But it is at once rendered turbid by bacteria if the supply of air ceases.

On account of the clearly demonstrated self-purification of the Isar, Von Pettenkofer declines to take upon himself to delay or complicate the domestic drainage and sewage of Munich, so important from a sanitary point of view, by the demand for irrigation fields, which is not easy to fulfil. He leaves to the future the installation of such fields, the use of which he does not deny, but the management of which should not be imposed upon the towns, but left to the agriculturists.

Von Pettenkofer concluded his lecture amidst general applause with the recommendation that the self-purifying power of rivers should be closely examined in as many places as possible.—*Chemiker Zeitung.*

Remarks on Hiepe's Paper "A New Use of Oxygenated Water in Analysis.—Mann (*Chemiker Zeitung*. —Hiepe regards the frequent presence of magnesium sulphate in oxygenated water as quite inexplicable. Mann informs him that oxygenated water prepared with barium dioxide contains barium chloride, which must be absolutely removed. In practice it is often eliminated by a cautious addition of magnesia.

NOTICES OF BOOKS.

The Perplexed Farmer: How is he to meet Alien Competition? Three Lectures, given at Brussels before the Belgian Royal Central Society of Agriculture, by GEORGES VILLE. Translated from the Fourth French Edition, with additional matter supplied by the Author, by WILLIAM CROOKES, F.R.S., V.P.C.S., &c. London: Longmans, Green, and Co.; and New York.

FOR a just appreciation of this work the reader will do well to bear in mind the first sentence of the Preface to the English edition. M. Ville's book does in fact consist of two portions, interwoven indeed, but so different in their character that the one part, the technical agricultural teachings, will be—or at least should be—warmly greeted by everyone who feels an interest in agriculture. Those who have met with the author's larger work, "Artificial Manures" (Longmans and Co.), will find the views laid down in that book here compactly re-stated, with all the additional weight which the experience of the last decennium has supplied In his former work the author insisted that among all the ingredients of an arable soil, four only—phosphoric acid, nitrogen, potassa, and lime—need to be constantly supplied, the others, though necessary, being always present in sufficience, if not in superabundance. Here it may be remarked that his teachings differ from English practice. We find nitrogen, phosphoric acid, and potassa always necessary, but we consider that lime is found in plenty in almost all soils. If it be contended that such lime may not be in a form available for vegetation, we reply that it is evidently dissolved by the rain and the carbonic acid of the atmosphere, as the springs and the streams of the limestone, and the chalk districts, are invariably "hard," from the presence of lime in solution.

But this matter does not call for discussion here. M. Ville, to meet some rather obsolete objections against chemical manures, shows the relation which they bear to farmyard manure. This substance, the alpha and the omega of traditional rule-of-thumb agriculture, is, in fact, like a chemical manure of very low quality.

Suppose we take 100 tons of farmyard dung, we find in it 80 tons of water, 13·29 tons of woody fibre, 5·07 tons of minerals which the soil does not need, and only 1·64 tons of the active matters—nitrogen, phosphoric acid, potash, and lime! Now it is evident that 1·64 tons of the really active matter can be bought for less money than the 100 tons of farmyard manure. Hence the farmer who buys and keeps up a stock of cattle merely or mainly to produce dung is painfully like an iron-master who should plant and maintain forests in order to supply his furnaces with fuel.

M. Ville must not be misunderstood. He does not decry cattle-feeding as a source of milk, meat, &c. He urges that the dung of animals kept for such purposes should be applied to the land after being duly fortified with phosphates, potash, or nitrogen, as it may be found needful for the requirements of any given crop. But he insists that farmyard manure is not a necessary factor for the production of crops, which can be grown as well, and often more economically, without it. Above all, he protests against the notion that matter obtains any mysterious occult value by passing through the bodies of animals. There is nothing in the dung which there was not in the food of the ox, horse, or sheep. And there is nothing in the food, be it grass, corn, or the like, which was not in the soil upon which the herbage, &c., grew. It is painful in these days to find agricultural authorities still advising farmers to buy "good feeding stuff" rather than superphosphate, salts of potash, sulphate of ammonia, or nitrate of soda.

But we must hasten on. Of the three substances—nitrogen, potash, and phosphoric acid—there is, according to M. Ville, or rather according to the facts of Nature, always some one which more especially influences some given crop, and which the author calls the *dominant* of that crop. Thus nitrogen, in the form of sulphate of ammonia or of saltpetre, is the dominant of wheat, hemp, and natural meadows; potash plays a corresponding part for peas, potatoes, lucerne, clover, and the vine. The dominant of the sugar-cane and the turnip is phosphoric acid, in the state of superphosphate, basic slag, &c. The ignorance or the neglect of this doctrine leads to much useless expenditure. Thus if we wish for a very fine crop of peas, and give accordingly a rich nitrogenous dressing, we do not recover the extra cost of the manure. If we add no nitrogenous manure at all, we get substantially as good a crop as if we had applied it. It may here be mentioned that peas, like many other leguminous plants, are able to appropriate the nitrogen of the atmosphere through the means of the small tubercles perceived on their roots, which abound with certain micro-organisms. More than this, upon clover, &c., the action of nitrogenous manures is actually hurtful.

A principle upon which M. Ville lays great weight, and which seems to have before it in agricultural practice a vast future, is "sideration." As every physicist knows, the sun pours down upon any given plot of land an amount of *vis viva* greatly in excess of the quantity actually utilised in the cultivation of the soil. By way of turning to account a part at least of this wasted energy, he advises that some of the plants which absorb the nitrogen of the atmosphere—such as clover—should be sown among corn or upon fallows. One or two crops of clover may thus be ploughed in, to the enormous increase of the fertility of the soil.

Another subject to which M. Ville has devoted his attention is what he calls *eugenism—i.e.*, the selection and varieties of plants which yield earlier, heavier, and more resistant crops than do others.

The work before us—setting aside the somewhat questionable political economy with which it is interwoven—is not only useful but profoundly suggestive, and deserves a careful study not only in the library, but in the experimental field. It is perhaps not too much to hope that M. Ville's labours may usher in a new era for agriculture.

A Theoretical and Practical Treatise on the Manufacture of Sulphuric Acid and Alkali with the Collateral Branches. By GEORGE LUNGE, Ph.D., Professor of Technical Chemistry at the Federal Polytechnic School, Zurich (formerly Manager of the Tyne Alkali Works, South Shields). Second Edition, Revised and Enlarged. Vol. I.—Sulphuric Acid. London: Gurney and Jackson. 8vo., pp. 940.

(FIRST NOTICE.)

IN the Preface of this work we find the following significant passage :—" The manufacture of chemicals has made enormous strides forward, both in quantity and quality, in France, and even more so in Germany. Many of the chemicals of these countries outstrip those of English works in purity, and their plant and their processes are frequently superior to those used in the majority of English works. Everybody knows how this has come about. The foreign chemists and manufacturers have looked all around, not merely in their own countries, but wherever they could find improved methods and apparatus, and upon the practical knowledge thus gained they have brought to bear the scientific training they had received at their universities and polytechnic schools. Thus they have already, in many fields formerly remunerative to British manufacturers, distanced the latter, immensely aided though they are by their long occupation of the ground, and by permanent natural advantages, such as cheapness of coal and freight." " This," he continues, " is likely to go on to an increasing extent if many British manufacturers decline to profit from a scientific study of their respective branches. This is all the less

excusable as England from of old has been a stronghold of scientific chemistry, and can hold its own against the whole world in that respect."

The moral involved in this passage does not need to be enlarged upon; it must be patent to every man who is not wilfully blind.

The present edition of Dr. Lunge's work is by no means a mere reprint of the former. Much that is now superseded has been eliminated, and is now merely referred to as to be found in the first edition. On the other hand, so much new matter has been added that the text is increased from 658 pages to 903 pages, and the engravings from 309 to 374, of which more than 150 are new. The author is in fact fully justified in calling it a new work, for which the first edition has served as the basis.

After giving a history of the manufacture of sulphuric acid, and a brief sketch of its general principles, the author passes to a survey of the raw materials employed. As regards brimstone, the Sicilian deposits still form the main source, though it is calculated that they will be exhausted in about sixty years. We find no mention of a large deposit of native sulphur said to have been discovered in New South Wales. By 1852 brimstone had been discarded in Lancashire in favour of pyrites, but it remained in use on the Tyne for a short time, though only on a small scale.

The British deposits of pyrites are not important either for quantity or quality. Cornish samples very rarely exceed 34 per cent of sulphur, and contain as much as 1·16 per cent of arsenic.

Irish pyrites are of more importance. They rarely exceed 35 per cent of sulphur, except those of Ovoca, which may reach 44 per cent. Irish ores are no longer burnt in England, on account of their exceedingly dense structure,—especially the yellow ore,—and it is very difficult to burn them reasonably clean, and even their analysis is a tribulation. The best pyrites of home origin is that from the Cae Coch Mine in Wales, which yields 48 per cent of sulphur, and is entirely free from arsenic. Unfortunately the supply is not large. It serves for manufacturing very pure oil of vitriol.

The most important German pyrites bed is at Meggen, in Westphalia. It is said to be quite free from arsenic— which Dr. Lunge queries—and to contain 47·5 per cent of sulphur. A drawback to the German ores is their proportion of zinc, which holds back a considerable quantity of sulphur in the state of sulphate. In Silesia 14 per cent is allowed as a maximum, and beyond this 1 per cent of sulphur is deducted on the invoice for each per cent of sulphur.

Norwegian pyrites contain mere traces of arsenic and burn clean, but they are in little favour, as their proportion of copper is too low to be worth extraction.

British acid-makers now principally burn Spanish and Portuguese ores from Huelva, the Rio Tinto, &c. These pyrites contain from 46 to 50 per cent of sulphur and from 3 to 4½ per cent of copper.

Dr. Lunge appropriately denounces the Cornish copper-assay, "a process of dry assaying only known to a few assayers living at Redruth and other places in Cornwall, the great inaccuracy of which is perfectly well known to all the parties concerned; it shows, for instance, only 2 per cent if 4 per cent are actually present. The price to be paid for the copper *in the ore*, by Cornish assay, is sometimes higher than the value of a similar quantity of copper *metal*. This remarkably irrational system has not hitherto been done away with for sales."

One of the greatest trials of a young chemist in the Lancashire district was to make his results, as obtained by modern accurate methods, coincide with those of this absurd process.

Many American pyrites have the advantage of being free from arsenic.

A very objectionable property of certain Spanish ores, as also of that from the Goshen Copper Mine, Co. Cork

is that they explode in the kilns and choke up the burners with fine dust.

The author explains why rich ores, wherever obtainable, have quite superseded poorer qualities. The cost of breaking and burning a ton, say, of 35 per cent ore, as well as the wear and tear of plant and the waste in the cinders, are as great as on a ton of a 45 per cent ore, whilst the returns are much less.

The instructions for the analysis of pyrites are full and excellent, and the attention of the operator is called to certain possible sources of error, such as the presence of nitric acid or a nitrite in the solution of the ore, and of ferric oxide or sulphate in the precipitate.

Department of Agriculture, Victoria. Report of the Department of Agriculture for the Year 1889—90. Bulletin No. 12. Melbourne: R. S. Bain.

THIS report is, upon the whole, highly satisfactory as showing an earnest desire to utilise the natural advantages of Victoria.

Mr. A. N. Pearson, F.C.S., the agricultural chemist to the Colony, is, with his two assistants and two pupils, busily engaged in the analysis of soils, manures, vegetable products, water, &c.; as also in experimenting on the preservation of fruits and milk, on the application of manures, and on the extermination of rabbits; 196 samples of soils, clays, &c., have been examined, 76 manures, 1586 samples of water, and 4 insecticides. The waters are classified as for irrigation, for domestic use, for farm and boiler work, samples of the Yarra water taken to decide its value for irrigating the Botanical Gardens.

Special attention is now being given to the growth of perfume plants, for which many parts of Australia are well adapted. The kinds of soil suitable for jasmine, tuberose, oranges, almonds, &c., are duly indicated. Soils are analysed free of charge, as are also manures if for farmers, but fees are charged to merchants and manufacturers.

Wattle bark from two-year-old trees was found to contain 46·47 per cent of tannin, whilst that from three-year-old trees gave 47·14. But the extract of the latter was the palest, which is of course an advantage both for dyeing and tanning purposes.

Experiments on the use of salicylic and boric acids for the preservation of foods led to condemnatory results.

Attempts are being made with a fair prospect of success to introduce the condensed milk industry. The native product is found richer in cream by nearly 3 per cent than the Swiss "Dairy Maid Brand."

Test-plots, for deciding the efficiency of manures, as proposed by M. Ville, are coming into favour.

We cannot express approval of the attempts to introduce the beet-sugar manufacture. There is plenty of land in Australia well adapted for the growth of the cane.

The entomologist to the department, Mr. A. N. Pearson, is fully employed in examining insects injurious to fruit-trees and experimenting on the diseases which they occasion. In this respect he works hand in hand with Mr. D. McAlpine, the vegetable pathologist and fungologist.

Much money and trouble are being expended in extirpating the Californian thistle, which has been introduced either by carelessness or criminal folly.

The cultivation of fruits is extending, and the produce is being exported to England both in the fresh, dried, bottled, and candied states. Australian fruits have the advantage that they reach English ports in late winter and spring, when European and American produce is scarce.

Butter, as an export from a sub-tropical country, may surprise us. But the value of the dairy industry in Victoria is given as above £3,000,000 annually, being more than the production of gold. Victorian butter is pro-

nounced by buyers in the London market second only to the best.

Attempts at the cultivation of dye-wares we can scarcely recommend. Many would doubtless grow to perfection in Victoria. But the demand for natural dyes has been so much reduced by the coal-tar industry that their cultivation could scarcely be remunerative. This is especially the case with madder.

CORRESPONDENCE.

BEHAVIOUR OF BUTYRIC ACID WITH ALKALINE PERMANGANATE.

To the Editor of the Chemical News.

SIR,—In reference to my previous note upon the above subject (CHEMICAL NEWS, vol. lxiii., p. 111) I have been induced to further investigate this extremely interesting question, for, as far as I am aware, it is the first recorded instance of the whole of the carbon being retained, no carbonic dioxide being produced in the reaction; and, further, because one of my critics went so far as to prognosticate that I should have to retract my statement, at the same time quoting from Beilstein's "Ag. Chem.," vol. i., p. 402, "that it was a well-known fact that butyric acid, when boiled with alkaline permanganate, resolved itself into carbonic acid" (*Analyst*, vol. xvi., p. 50).

Coincident with the above, Mr. A. H. Allen has introduced me as an authority to the members of the British Association, at their Cardiff Meeting (as reported in the CHEM. NEWS, vol. lxvi., p. 179) as follows:—"That it was erroneous was already rendered extremely probable by *Mr. Hehner's failure* to obtain any traces of oxalic acid from butyric acid by treatment with permanganate" (CHEM. NEWS, vol. lxiv., p. 182).

In the *Zeitsch. f. Angew. Chem.*, 1891, p. 400, there is an article headed "The Estimation of Glycerol by Benedikt and Zsigmondy's Method," by C. Mangold. The author, after describing his simplifications of Benedikt and Zsigmondy's method, goes on to state " Butyric acid yields oxalic acid only when boiled for a considerable time with an excess of alkali and potassium permanganate,"—exactly what I have already announced, and the discoverer of this eccentric but wonderful reaction has his work unexpectedly confirmed. The question does not even end here, for in the August number of the official Journal of a semi-trade society there appears an abstract of C. Mangold's paper already referred to; but all mention of the formation of oxalic acid from butyric acid, in the manner described, is carefully suppressed, the abstractor's initials being O. H.

Mr. Allen charges me with having stated that " *tallow* required 23 per cent of caustic potash (KHO) for its saponification, against 19·3—19·8 per cent as the united experience of numerous other observers " (CHEM. NEWS, lxiv., p. 182). I never said or wrote anything of the kind; the statement is purely a misrepresentation He quotes me as an authority to support his own opinions, when it suits himself; the next minute he abuses me. He also refers to the bichromate method for the estimation of glycerin, but the same objection applies to it, as later research has proved conclusively that butter contains a volatile fatty acid which readily reduces acid bichromate, not to mention castor oil, which is said to contain iso-butyric acid,

The butyric acid and permanganate reaction is extremely interesting and also eccentric, but with care theoretical results can be obtained; and in saying *Au revoir* to my critics I have nothing to retract; it is they who must again recant.—I am, &c.,
           WILLIAM JOHNSTONE.
13, Fish Street Hill, E.C.,
   October 10, 1881.

MR. ALLEN AND THE ISOGLYCERIDE THEORY.

To the Editor of the Chemical News.

SIR,—From the report of Mr. Allen's paper published in the last number of the CHEMICAL NEWS, I perceive that in my absence from the meeting of the British Association that gentleman has made a very extraordinary statement, which would not have passed unchallenged in my presence. I quote the following passage: " I believe Messrs. Wanklyn and Fox have never published a single original experiment in support of their assertion that the proportion of glycerin yielded by saponification of butter and other fats exhibits any grave departure from the amount required by the accepted views of their constitution."

Now, so far from there being any ground for that statement of Mr. Allen's, the very reverse is notoriously true. At a meeting of the Society of Chemical Industry I did publish an original experiment in support of my view, and, strange to say, Mr. Allen was present, and actually took part in the discussion. The paper was published by the Society of Chemical Industry, and the following is an abstract. I operated upon 50 grms. of dry butter-fat, and saponified with a weighed excess of lime, proving that saponification was complete by showing that the lime had absolutely lost its causticity, and that the butter had ceased to exist as butter, inasmuch as 300 c.c. of boiling alcohol dissolved no butter out of the residue; and having proved that complete reaction had taken place I sought for the resulting glycerin, and obtained only 3·1 grms. instead of double the quantity, as the commonly received theory requires. I believe that chemists will find great difficulty in resisting the conclusion which follows from this experiment. Whether Mr. Allen will be satisfied by it I cannot tell; but until he has given some explanation of the extraordinary assertion which I have quoted, I shall consider myself relieved from the necessity of noticing anything else in his paper which deals with a subject on which I possess special information.—I am, &c.,
           J. ALFRED WANKLYN.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxiii., No. 13, September 28, 1891.

This issue contains no chemical matter.

Moniteur Scientifique, Quesneville.
Series 4, Vol. iv., Part 2, No. 587.

Determination of Minute Quantities of Aluminium in Irons and Steels.—J. E. Stead.—From the *Journal of the Society of Chemical Industry.*

New Method for Determining Aluminium in Ferro-Aluminium and Steel. — A. Ziegler (*Dingler's Journal*).—This paper will be inserted in full.

New Process for Determining Pure Glycerin in Commercial Glycerin.— C. and Ch. Deiss (*Romen's Journal*).—This process is founded upon the fact that a given mixture of glycerin and phenol always absorbs the same quantity of water. The weight of water absorbed is proportional to the degree of concentration of the glycerin employed. To make a determination, we place in a beaker holding about 100 c.c. a mixture of 10 grms. of

the glycerin in question and 6 grms. of pure crystalline phenol. Then we drop in by means of a Mohr's burette a solution of 50 grms. of phenol and 1 litre of distilled water until there appears, on stirring, a permanent turbidity. Pure anhydrous glycerin requires to produce this result 28·15 c.c. The authors have remarked that for each additional per cent of water in the sample the number of c.c. employed diminishes by 0·39 c.c. So that if we call 9 the number of c.c. used, the quantity of water per cent will be shown by the formula $\frac{29·15 - 9}{0·39}$. It is preferable to operate at the temperature of 11°.

Titration of Formaldehyd by means of Ammonia. —W. Eschweiler (*Chemiker Zeitung*).—G. Losekann has recently pointed out that when titrating formaldehyd with ammonia we must remember that the hexamethylene-amine formed can, in its quality of monacid base, take possession of a part of the acid by means of which we titrate the excess of ammonia. The quantity of ammonia which disappears would be for 6 mols. formaldehyd, not 4 mols., but only 3; one mol. of the acid used for the titration being neutralised by the hexamethyleneamine formed. According to the author, this assertion is inaccurate if we use methyl orange or cochineal as indicator. If we use litmus, we must not take account of the acid corresponding to the hexamethyleneamine.

Determination of Indigo for Industrial Use.—F. A. Owen (*Romen's Journal*).—One grm. of the product is dried at 100°, and the loss of weight is determined. It is then ground as finely as possible in a glass mortar, water is added, and it is rubbed up to a thin paste, which is introduced into a a flask of 250 c.c. There are then added 3 grms. of zinc powder and about 6 grms. of caustic soda, the flask is filled up to the neck and agitated from time to time. After from half an hour to two hours the reduction is complete, when the liquid should be green. Fifty c.c. are then taken with a pipette, and exposed to the air for half an hour. The indigo is then thrown down with hydrochloric acid, collected upon a filter, dried at 100°, and weighed.

Researches on the Procedures for Determining Albumenoid Substances, with especial reference to Milk.—J. Sebelien.—From the *Bulletin de la Société Chimique*.

Agricultural Analyses.—H. J. Patterson.—From the *American Chemical Journal*.

Artificial Colouring Matters considered with reference to their Poisonous Properties.—This treatise does not admit of useful abstraction.

MISCELLANEOUS.

Spectroscopic Analysis.—Prof. Ostwald (*Chemiker Zeitung*), in a discourse on the progress of Physical Chemistry, delivered before the Congress of German Naturalists and Physicians, declared that, owing to the recent investigations of Baluezs, Deslandres, Kayser, Runge, and others, results have been reached which justify the most sanguine hopes. It is generally believed that all substances are dissociated in the electric arc into their elements, and that thus a spectrum of their components is obtained. All substances which are formed with absorption of heat become more permanent as the temperature rises, and inversely. In many instances this inverse case occurs, but it cannot be assumed as the universal and sole course of the phenomena.

Use of Lupins, Horse Chestnuts, and Acorns as Human Food.—At the recent Congress of German Naturalists and Physicians, P. Soltsien (*Chemiker Zeitung*) recommended the use of ammonia at 10 per cent as a suitable agent for removing tannin and poisonous alkaloids. Horse chestnuts and acorns must be previously comminuted. As lupins contain no starch, it should be

added to the purified product in the shape of ground acoros. The attempts at utilising horse chestnuts (essentially removal of sapotoxine) are not very satisfactory, as the loss of substance is very considerable. Fragments of the rind must also be removed, as they contain much tannin. Attempts to make horse chestnuts edible by roasting have not yielded good results; the sapotoxine is certainly destroyed, but the nuts cannot be eaten, as the fatty oil takes an unpleasant taste on roasting. The results which the author obtained in removing the bitterness of acorns are noteworthy. In addition to the ammonia process he obtained good results by extracting the acorns six to eight times with cold soft water, and drying immediately afterwards. The loss by this method is still too great (25 per cent), consequently Soltsien prefers to make the acorns up into a paste with milk, and allow them to ferment. The elimination of bitterness by this process is substantially perfect, and loss is avoided. Acorn meal so prepared costs at most 4d. per kilo.

Self-Acting Apparatus for Shutting-off Gas-Flames.—J. Hartkorn (*Chemiker Zeitung*).—An intermediate flask is inserted in the gas-piping from which the gas reaches the flexible tube, passing to the burner through a long glass tube sliding in the stopper. Into the flask water flows with a known speed from a cistern placed at a higher level. As soon as the level of the latter reaches the lower end of the exit gas-pipe the latter is closed and the flame is extinguished.

Action of Organic Compounds upon the Alkaline Sulphohydrates.—F. Fuchs (*Monatshefte*).—The view expressed by the author in an earlier paper, that also in the oxy-acids of the fatty series only the hydrogen of the carboxyl group is replaced by a metal on treatment with an alkaline hydrosulphate, has been found fully confirmed by experiments on malic and tartaric acids. The halogeniferous monatomic phenols do not seem to act as acids.

Recognition of Diresorcine in Synthetic Phloroglucine.—J. Herzig and F. Zeisel (*Monatshefte fur Chemie*).—A few milligrms. of the phloroglucine in question are treated with 1 c.c. of concentrated sulphuric acid, 1 to 2 c.c. of acetic anhydride are added, and the whole is heated for five to ten minutes in a boiling water-bath. In presence of diresorcine, there appears a fine violet-blue colour. By means of this reaction, 0·4 per cent of diresorcine can be detected in phloroglucine. Pure phloroglucine, from maclurine, or obtained by means of the acetate method, or of Skraup's process, are perfectly free from diresorcine, whilst commercial phloroglucine always gives the above reaction.

Araeometer for Complete Submersion.—N. Reggiani (*Atti dei Lincei*).—In this instrument the surface tension of the liquid does not interfere. Glass bodies may be loaded with platinum rings so that they remain suspended in the liquid. Or for certain purposes the author uses hollow glass globes of known specific gravity placed in the liquid in question, which is then diluted with water until the balls remain suspended. In this case corrections are needed both for the temperature and the contraction in volume occasioned on mixing the liquids.

THE CHEMICAL NEWS.

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A METHOD FOR THE SEPARATION OF ANTIMONY FROM ARSENIC
BY THE SIMULTANEOUS ACTION
OF HYDROCHLORIC AND HYDRIODIC ACIDS.

By F. A. GOOCH and E. W. DANNER.

A METHOD for the separation of arsenic from antimony based upon the difference in volatility of the lower chlorides was introduced originally by Fischer.[*] This method of treatment consisted in the reduction of the chlorides by means of ferrous chloride and the volatilisation of the arsenic by repeated distillations of the mixture with hydrochloric acid of 20 per cent strength added in successive portions. The process has been subsequently modified by Hufschmidt[†] by the substitution of gaseous hydrochloric acid, introduced in continuous current into the distilling mixture, for the aqueous acid, and later changed further and improved by Classen and Ludwig,[‡] who employ ferrous sulphate, or ammonio-ferrous sulphate, in place of the less easily prepared ferrous chloride. In its latest form the method is exceedingly exact, but the conditions are such that the antimony in the residue must be determined gravimetrically. It has been our endeavour to so arrange the process that the determination of the antimony may be made by a rapid volumetric method, and this we have attempted to accomplish by substituting for the iron salt, which utterly precludes the direct volumetric estimation of the antimony, another reducer—hydriodic acid—which can interfere in no way with the subsequent determination of the antimony by the well known iodometric method.

It has been shown in previous work in this laboratory that arsenic[§] and antimony[||] may both be reduced by the action of hydriodic acid applied under appropriate conditions. In those processes, however, it was essential that the arsenic should not volatilise, and the conditions were adjusted accordingly. In the present case we have to test the reducing action of hydriodic acid in the presence of strong hydrochloric acid and at the boiling temperature of the solution, — conditions arranged to bring about the volatilisation of the arsenic as rapidly as possible. Certain preliminary experiments gave indication that a $\frac{1}{2}$ grm. of arsenic oxide could be completely volatilised by the action of potassium iodide in excess in the manner described, and that an equivalent weight of antimonious oxide (added in the form of tartar emetic) was retained entirely in the residue under similar conditions of treatment. Moreover, it appeared that this action could be brought about in solutions measuring no more than 100 c.m.[3] at the beginning and no less than 50 c.m.[3] at the end of the distillation, so that a very considerable saving of time over that demanded by the process of distillation, as left by Classen and Ludwig, could be effected. Accordingly we proceeded to test the action of the hydriodic acid quantitatively, following the same general lines. The distillation apparatus consisted of a flask of 250 c.m.[3] capacity, provided with a hollow glass stopper tightly fitted in a ground joint, the stopper itself being sealed upon a large glass tube bent suitably to connect the interior of the flask with an upright condenser, while through the hollow stopper, and sealed into it, passed a smaller glass tube reaching nearly to the

bottom of the flask. The arrangement was such that a current of gas entering the smaller tube would pass nearly to the bottom of the flask, and then out through the hollow stopper into the condenser, without meeting joints of rubber or cork. Into this flask was weighed, for the experiments of Table I., about a $\frac{1}{2}$ grm. of carefully re-crystallised tartar emetic, and a $\frac{1}{2}$ grm. of pure dihydrogen potassium arseniate and a grm. of potassium iodide were added in concentrated solution, the volume of liquid being made up to 100 c.m.[3] by the addition of strong hydrochloric acid. A brisk current of hydrochloric acid gas was passed into the solution through the tube sealed into the glass stopper of the flask until complete saturation was effected, and then the liquid was heated and distilled in the continuous current of hydrochloric acid gas until the volume of 30 c.m.[3] was reached. Iodine was evolved as soon as the liquid became warm and the greater part of it passed into the distillate with the first 10 c.m.[3] When the final concentration was reached the solution was in each case colourless, but on cooling there appeared in one of the two experiments of this set a pale yellow tint, which vanished with the dilution involved in the transfer and washing from the flask previous to titration. The addition of starch to the cooled and diluted liquid developed no colour. To the liquid were added 1 grm. of tartaric acid, to keep the antimony in solution during subsequent treatment, sodium hydrate nearly to neutrality, and hydrogen sodium carbonate in excess amounting to about 20 c.m.[3] of the saturated solution; and the antimonious oxide in solution was titrated by decinormal iodine standardised against tartar emetic. The details of these experiments are given in Table I.

In Table II. are comprised the accounts of experiments similar in general to those of Table I., excepting that the final volume after concentration was a little more, and the antimony was in every case oxidised in alkaline solution by standard iodine previous to the introduction of hydrochloric acid and distillation.

Table III. includes the records of experiments similar in every respect to those of Table II., excepting that, as starch showed a slight colour in the cooled liquid after distillation, the solution was treated with an excess of sulphurous acid which was subsequently oxidised exactly by standard iodine previous to neutralisation and the final titration.

The same general phenomena were observed in all these experiments, and deficiencies in the amounts of antimony indicated, whether the element was present in the lower or higher degree of oxidation before distillation, appear in all, but most notably in the results of Tables I. and II. These losses cannot be attributed, entirely at least, to mechanical transfer in the process, inasmuch as the greater losses are not associated with the greater concentrations; and, furthermore, according to our qualitative experiments made under the conditions of these determinations, no antimony, so far as we could observe, passes into the distillate. If the colouration of the liquid on cooling were due to the liberation of iodine by the action of air upon the hydriodic acid, the iodine thus set free might be counted upon to oxidise a corresponding portion of the antimony in the neutralisation, and so to occasion a deficiency in the indications of titration. Against this supposition, however, we have the evidence of experiment that the greatest losses are not found in those cases in which colour was developed in the cooling liquid. Moreover, in all cases, excepting those of Table III., starch gave no test for free iodine in the diluted liquid, though it must not be overlooked that the presence of a considerable amount of hydrochloric acid tends to impair the delicacy of the test. If, on the other hand, the colour is not due altogether to free iodine, it is difficult to account for its development, unless it is caused by the formation of antimonious iodide as the solution of strong hydrochloric containing also hydriodic acid cools. On the whole, we are inclined to attribute at least a part of the apparent deficiency to the presence, at the time of

* *Ann. Chem. u. Pharm.*, 208, 182.
† *Ber. d. Deutsch. Chem. Ges.*, xvii., 2245.
‡ *Ibid.*, xviii., 1110.
§ Gooch and Browning, *Amer. Journ. Sci.*, xl., 66.
|| Gooch and Gruener, *Ibid.*, xlii., 213.

Table I.

H_2KAsO_4 taken. Grm.	KI taken. Grm.	Volume Initial. C.m.³	Final. C.m.³	Colour On cooling.	With Starch.	Sb_2O_3 taken. Grm.	Sb_2O_5 found. Grm.	Error. Grm.
0·5	1·0	100	30	Pale yellow	None	0·2282	0·2271	0·0011 —
0·5	1·0	100	30	None	None	0·2283	0·2066	0·0017 —

Table II.

0·5	0·5	120	50	None	None	0·2258	0·2235	0·0023 —
0·5	0·5	100	50	Pale yellow	None	0·2252	0·2235	0·0017 —
0·5	0·5	100	50	Pale yellow	None	0·2178	0·2163	0·0015 —
0·5	0·5	100	50	Trace	None	0·2231	0·2231	0·0000
0·5	0·5	100	40	Trace	None	0·2261	0·2235	0·0026 —

Table III.

0·5	0·5	100	50	Pale yellow	Faint	0·2268	0·2265	0·0003 —
0·5	0·5	100	50	Pale yellow	Faint	0·2306	0·2300	0·0006 —
0·5	0·5	100	50	Pale yellow	Faint	0·2272	0·2264	0·0008 —

neutralisation, of a small amount of iodine chloride, which, in accordance with what is known of its modes of formation, might be formed by the oxidising effect of the antimonic and arsenic oxides upon the mixed acids. At all events, it is evident that if iodine chloride were present we should expect to note the phenomena which we do see; it would give, in small quantity, little or no colour to the liquid, would not show the starch reaction for free iodine in the acid solution, and would be destroyed with the formation hydrochloric and hydriodic acids by the addition of sulphurous acid to the still acid liquid, leaving the antimony unchanged and determinable iodometrically in alkaline solution after the exact oxidation of the excess of sulphurous acid by iodine in acid solution; on the other hand, it would act in alkaline solution like the free halogens, and tend to diminish the antimony indicated by titration. Whatever the real cause or causes of the deficiency may be, it appears, in the results of Table III., that the treatment with sulphurous acid affects the indications favourably. The mean error of three closely agreeing determinations is 0·0006 grm., and this is plainly within the limits of allowable variation in iodometric work with decinormal solutions.

It appears, therefore, that hydriodic acid may be made to serve satisfactorily as a substitute for the ferrous chloride of Fischer's original method, or for the ferrous sulphate of the modification of Classen and Ludwig, the determination of the residual antimony being perfectly practicable. The method of proceeding which we advocate is briefly summarised in the following statement:—
To the solution of the oxides of arsenic and antimony, taken in amounts not exceeding 0·5 grm. of each, potassium iodide is to be added in a little more than the equivalent quantity, and enough strong hydrochloric acid to raise the entire volume of the solution to 100 c.m.² Hydrochloric acid gas is passed into the liquid to saturation as well as during the distillation to follow, and the distillation is carried on until the volume of the liquid decreases to 50 c.m.³ or a little less. The liquid is cooled rapidly, treated first with an excess of sulphurous acid, and then with iodine to the exact oxidation of the former reagent; and, after the addition of 1 grm. of tartaric acid to every 0·2 grm. of antimonious oxide, the acid present is nearly neutralised with sodium hydrate, the neutralisation being completed by hydrogen sodium carbonate added in excess to an amount corresponding to 10 c.m.³ of the saturated solution for every 0·1 grm. of antimonious oxide present. Titration with decinormal iodine standardised against tartar emetic gives the antimony quickly and with a fair degree of accuracy. The whole process requires about an hour and a half for completion.

A New Washing-Bottle.—V. Hybinetto.—Referring to the description of a washing-bottle (*Zeit.*, xxx., p. 591) the author states that he has used such an apparatus for some years.

THE SEPARATION OF RESIN FROM FATTY ACIDS.

By J. ARTHUR WILSON.

THE detection of resin and its separation from fats and oils was at one time a very difficult problem to the analyst, and in many cases was impossible. Amongst many processes we have those of Henderson, Barfoed, and Gladding, the latter of which has found the greatest favour. It suffers from one very serious defect, however, and that is the correction for solubility of the fatty acids and silver salts in ether. This is a very variable factor, and, of course, is dependent on the nature of the fatty matter used in the fabrication of the soap. With small quantities of resin the error thus introduced may be as much as 20—30 per cent, but of course in soaps of high resin content—say 20 per cent—the error diminishes.

Mr. R. Williams (*Analyst*, vol. xv., p. 169) obtained very good results by the process; thus, in a soap which actually contained 30·0 per cent of resin, he obtained 30·7 per cent, but no mention is made as to whether the amount remaining in the lyes, after precipitation of the soap, was determined. As to the simple detection of resin, no doubt the best test is to boil the dry fat or fatty acids (10 drops) with 5 c.c. acetic anhydride, cool, and add 2 drops of pure sulphuric acid (1·84 specific gravity), when the reddish violet colour due to resin is easily observed, 1 per cent of which can thus be detected.

It seems that all the above processes must make way for the admirable process of Twitchell (*Analyst*, Oct., 1891), who found that whereas fatty acids are, as is well known, converted into neutral ethers on passing dry hydrochloric acid gas into their alcoholic solution, the acids constituting resin are not attacked. The process obviously may be either gravimetric or volumetric, but chemists will prefer the latter on account both of speed and accuracy. The description of the process is as follows:—2·5 to 3 grms. of the dried fatty and resin acids are dissolved in from 25—30 c.c. of perfectly absolute alcohol, and a current of dry hydrochloric acid gas passed in constantly. The flask containing the mixture must be kept cool by immersion in cold water. When the etherification is complete the ethers separate and the gas is no longer absorbed. The flask is removed, corked well, and allowed to stand half an hour. It is diluted with about 100 to 125 c.c. hot water, then cooled, transferred to a separatory funnel, and agitated with 75 c.c. of ether. The watery layer is removed, and the ethereal layer washed with cold water till neutral to delicate litmus solution (twice always is sufficient). The ethereal liquid is received in a flask, the separator washed out with about 50 c.c. of neutral spirit, and the whole titrated by standard alcoholic alkali, using phenolphthalein as indicator. The alkali should be standardised by an accurate solution of half normal HCl, and should be either one-fifth or one-half normal

according to the amount of resin in the fatty acids. Taking the mean combining weight of resin as 347, then the percentage is easily calculated; it is reported both on 100 of dry fatty matter and on 100 of soap.

Twitchell's test experiments are eminently satisfactory, and I have now pleasure in confirming them by my own tests :—

1. Sample of distilled fatty acids containing no resin, when treated as described, showed 0·7 per cent resin.

2. The above distilled fatty acids, to which were added common resin to the extent of 22·5 per cent, showed, when treated as above described, 23·3 per cent of resin, which, after deducting the 0·7 per cent found in No. 1, gives exactly 22·5 per cent, or the amount which was added.

3. Soap made from palm oil and other fats, but no resin, gave 0·8 per cent resin.

4. Another soap made from fatty matter of unknown origin, but no resin, gave 1·0 per cent resin. This, it should be observed, was of a dark colour, and evidently contained some altered or oxidised oily matter.

5. Soap which showed by Gladding's test 6 per cent of resin, gave 4·9 per cent by Twitchell's process.

The above results are all that may be desired, and I have now to show how the process may be still further shortened without any sacrifice of accuracy. This can be done by leaving out the washing and dissolving in alcohol direct. A few drops of methyl orange are then added and alkali till neutral to this indicator; phenolphthalein is then added, and the titration completed as before. The alkali required in the first case is for the neutralisation of the free hydrochloric acid, and is of course neglected. That required to neutralise to phenolphthalein is of course due to the resin, and is calculated as such.

Tottington Mills,
    Oct. 6, 1891.

THE ESTIMATION OF COMBINED ALKALI IN SOAP.

By J. ARTHUR WILSON.

THE writer, who was the first to point out the error attendant on the use of the alcohol method of determining free caustic alkali in soap (CHEMICAL NEWS, vol. lix., p. 280; *Jour. Soc. Chem. Industry*, vol. viii., p. 479), advised, when both free fat and free caustic alkali are present simultaneously, the adoption of the following method :—

Determine, firstly, the total alkali in the usual manner. Then determine the amount of alkali required to neutralise the isolated fatty and resin acids from a weighed quantity of the soap. Obviously the difference is the alkali present as hydrate, carbonate, or silicate of soda, &c. In the same paper above mentioned the following sentence occurs :—" Supposing palm, nut, or cocoanut oil to have been used in the fabrication of the soap, the determination of the Na₂O required to neutralise the fatty acids becomes inaccurate, owing to the solubility of the lower fatty acids; hence another complication arises. The error, of course, may be of greater or less extent, according to the nature of the fatty matter of the soap." Fortunately, this error can be completely excluded by operating in a very simple manner as follows :—

1. The alkali, in all forms, is determined by titration with standard acid in the usual manner.

2. Another weighed quantity of the soap is decomposed in an Erlenmeyer flask with a slight excess of dilute H_2SO_4, and the flask kept on the water-bath till the fatty acids separate quite clear. The flask is then placed in ice water to cool, and then filtered. The fatty acids are washed three times successively with 250 c.c. of boiling water and allowed to cool each time and filtered. The united filtrates are diluted to 1 litre, and 500 c.c. placed in a clear white beaker and tinted with methyl orange; N/10 alkali is then dropped in till the liquid acquires the usual colour, after which a little phenolphthalein is added, and the addition of standard alkali continued till a permanent pink is established. The number of c.c. used in the latter titration are due to the soluble acids, and are calculated to caprylic acid. The fatty acids in the flask, and any little on the filter, are dried and weighed, and then dissolved in alcohol, and titrated with N/2 alcoholic alkali. The alkali so used, *together with that required for neutralisation of the soluble acids,* and deducted from the total alkali, gives the alkali existing in other forms than as soap.

Of course, if desired, the soap may be decomposed with standard H_2SO_4, and the alkali required to neutralise the methyl orange noted, which, deducted from the total acid used, would give the acid equivalent to the alkali existing in all forms. In this manner we get—

Total alkali   .. .. ..
Combined alkali . .. ..
Insoluble fatty acids   ..
Soluble   „   „   ..

The following examples illustrate the method :—

No. 1—*Soap from Cocoanut Oil and other Fats (Highly Watered).   Total Alkali by Titration, 2·06 per Cent* Na₂O.

Weight of soap taken .. .. .. 17·145 grms.
Weight of insoluble fat acids .. 2·29 „ = 13·35%
C.c. of N/2 alkali to neutralise .. 16·1 „ = 8·05 normal.

C.c. of N/10 alkali to neutralise
soluble acids .. .. 4·2 „ = 0·42 normal

C.c. of N/10 alkali to neutralise soluble acids 4·2 = 0·42 normal = 0·36 per cent soluble acids (= caprylic).

Total alkali used for both soluble and insoluble fatty acids, c.c., = 8·47 normal.

$$\frac{8·47 \times 0·031 \times 100}{17·145} = 1·53 \text{ per cent combined alkali.}$$

	Per cent.	
Total alkali (Na₂O) ..	2·06	
Combined alkali (Na₂O)	1·53	
Uncombined	0·53	
Soluble fatty acids ..	0·36	= caprylic.
Insoluble „ „	13·35	
Total fatty acids	13·71	

No. 2.—*French Scouring Soap.   Total Alkali by Titration, 7·037 per Cent.*

Weight of soap taken .. .. .. 5·889 grms.
Weight of insoluble fatty acids .. 2·005 „ =34·06%
C.c. of N/2 alkali to neutralise .. 18·05 „ = 9·025 normal.

C.c. of N/10 alkali to neutralise soluble acids, 10·7 = 1·07 normal = 2·6 per cent caprylic acid.

Total alkali used for both soluble and insoluble acids = 10·1 c.c. normal = 20·2 N/2.

$$\frac{20·2 \times 0·0155 \times 100}{5·889} = 5·32 \text{ per cent combined alkali.}$$

	Per cent.	
Total alkali (Na₂O) ..	7·037	
Combined alkali	5·32	
Uncombined..	1·717	
Insoluble fatty acids ..	34·06	
Soluble „ „ ..	2·6	= caprylic.
Total „ „ ..	36·6	

Tottington Mills, October

SEPARATION AND DETERMINATION OF TELLURIUM.

By E. DONATH.

In the determination of tellurium by the older method generally followed — precipitation from a hydrochloric solution with sulphurous acid in heat—a complete separation is effected, but the process is very tedious. After heating for some hours, and on addition of sulphurous acid in excess, slight separations of tellurium are still obtained in the concentrated filtrates. H. Rose's statement, that the separation by means of sulphurous acid is not more tedious than that by means of sodium thiosulphate, is confirmed by Donath.

In precipitating tellurium by glucose in a boiling alkaline solution, as proposed by Stolba and used by Lad. Kästner, the separation is complete and soon effected. The deposit of tellurium can be either weighed on a tared filter or dissolved off the filter by dropping upon it nitric acid, moderately diluted and heated (2 parts nitric acid and 1 part water, with a few drops of sulphuric acid). The solution is then concentrated in a small porcelain capsule, and the residue, after gentle ignition, is weighed as tellurous acid, TeO_2.

The author's proposed method—precipitation by stannous chloride or an alkaline solution of stannous oxide—led to no satisfactory results. The separation in an acid solution by means of hydrosulphurous acid was quite successful. A solution of this acid can be easily and rapidly prepared by digesting zinc clippings with aqueous sulphurous acid, or by covering the clippings with a concentrated solution of sodium bisulphite and cautiously acidulating the solution with a little hydrochloric acid. The deep yellow solution thus obtained, which must be filtered before using, precipitates tellurium at once in the cold, and, if not too dilute, in the form of flocks which subside readily. If the hydrosulphurous acid is not decomposed, the tellurium is separated as such; if the liquid is heated, and even otherwise, in consequence of the almost inevitable decomposition of the hydrosulphurous acid, the tellurium subsides mixed with tellurium sulphide, and the liquid becomes opalescent in consequence of finely suspended sulphur. In concentrated hydrochloric solutions and with a suitable excess of hydrosulphurous acid the precipitation is complete after heating for fifteen minutes. The washed precipitate is rinsed through the perforated filter into a tared capsule, a little concentrated acid is added, the solution is evaporated down, and the residue, after slight ignition, is weighed as tellurous acid.

This rapid process has the disadvantage that it is impracticable in presence of many metallic oxides. Thus, salts of bismuth are precipitated by hydrosulphurous acid at common temperatures, and on heating the liquid other metals of the H_2S group are precipitated by the hyposulphurous acid formed on the decomposition of the hydrosulphurous acid.

On using a pure solution of an alkaline tellurite, concordant and accurate results were obtained by precipitation with glucose in an alkaline solution, and with hydrosulphurous acid in an acid solution.

The opening up of products, or minerals containing tellurium, and its separation from accompanying elements, were attempted by the author in various manners. After many fruitless experiments, he succeeded in developing a method which meets all fair demands as regards accuracy and despatch.

About 3—4 grms. of the very finely pulverised sample are gradually oxidised in a porcelain capsule with a minimum of concentrated nitric acid, and the thick pasty mass is heated until all excess of nitric acid is eliminated. The temperature must not be raised high enough to decompose the less stable iron, copper, and bismuth nitrites. In this case, there would be formed from the tellurous acid, telluric acid; and, subsequently, very sparingly

soluble tellurates, the formation of which must be avoided. The dry mass obtained is ground finely in the capsule with an agate pestle, and moistened with concentrated soda-lye, which becomes strongly heated by the transformation of the nitrates. After digestion for thirty minutes, a little more soda-lye and a corresponding quantity of water are added, the liquid is filtered off, and the tellurium is precipitated in the filtrate by boiling for at most twenty minutes with a pure solution of glucose, and it is either determined as such or as tellurous acid.—*Zeit. Anal. Chemie.*

DETECTION OF ADULTERATIONS OF BASIC SLAGS.

By DR. MORGAN.

In the Agricultural Section of the German Congress of Naturalists and Physicians the author pointed out various methods for the qualitative detection of adulterations in basic slag. The loss on ignition is important. If the sample is genuine there is no loss. If it amounts to ½— 1 per cent, the sample is almost always adulterated. The determination of the specific gravity also gives a clue, especially in the case of sophistication with redonda phosphate. The author does not use for this determination a solution of mercuric potassium iodide, but bromoform (specific gravity = 2·9).

Treatment with dilute soda-lye separates redonda phosphate and basic slag. If there is an impurity of redonda phosphate a very copious precipitate is produced.

If the coarsely ground sample is examined yellow particles are found if redonda phosphate is present, but not in case of a pure basic slag.

The best method for a quantitative determination is that of Jantsch and Schucht. The P_2O_5 of basic slag is perfectly soluble in 5 per cent citric acid, but not that of redonda phosphate.

"Taffin" slag behaves like basic slag, but it remains suspended in bromoform. Dr. Loges, of Posen, mentioned a new spurious material said to be of English origin. The small sample which he had obtained contained 4 per cent caustic lime, 6·4 per cent calcium carbonate, as well as calcium fluoride. It is probably sophisticated with Welsh phosphate.—*Chemiker Zeitung.*

DETECTION OF FORMLESS FERMENTS AND POISONS IN BLOOD.

PROF. R. KOBERT.

Both the physiological and the chemico-legal demonstration of unstable poisons in blood encounter difficulties depending mainly on the fact that the colouring-matter of the blood (if the red globules are dissolved by putrefaction, morbid processes, or improper treatment such as the addition of water), forms a tarry mass which it is difficult to treat chemically and which is perfectly useless for physiological experiments. The removal of this tarry colouring-matter is generally effected by plentiful dilution and boiling with acetic acid, or precipitation with alcohol, with potassium ferrocyanide and acetic acid, or with uranium nitrate.

In all these cases the serum albumen present in the blood along with the blood-pigment as well as all albumenoid enzymes and toxalbumens are simultaneously precipitated, and thus the detection and the isolation of the enzymes and toxalbumens is rendered impossible. But if we had an agent which would throw down the colouring-matter of the blood, leaving all other substances in solution, and chemically unaltered, we should have made

an important step towards the isolation and detection of the enzymes and toxalbumens.

Zinc-powder may be regarded as such a precipitant for hæmoglobine. In forensic chemistry which is generally concerned with stale, offensive blood, this agent has the advantage that it renders the specimen almost inodorous even if several weeks old. The completeness of the precipitation is not interfered with by the age of the blood. The following conditions are essential for successful precipitation :—

1. In quite recent blood, freshly drawn from normal men or other animals, which is always alkaline, the alkalinity must be neutralised before the addition of the zinc powder. The same holds good of the blood of dead bodies a week old in which ammonia has been formed. On exposure to the air, or remaining in the body, the normal alkalinity of the blood is lost within 1 to 2 days. Diseases—especially fevers—often reduce the alkalinity before death to such a degree that the zinc may be added directly.

2. The blood must be free from methæmoglobine. If this substance is present the blood is allowed to remain in an open vessel without dilution or shaking until the last trace of methæmoglobine has disappeared. It is known that this disappearance often ensues within 24 hours, whether in the corpse or in jars, even when the original quantity of methæmoglobine was very considerable.

3. The blood must be diluted with at least 3 to 5 volumes of water.

4. The zinc-powder must be as pure as possible, containing nothing but zinc and zinc oxide.

5. The quantity of the zinc-powder must be equal to a quarter or a half of the original weight of the blood.

6. The mixture must be energetically shaken for a considerable time.

If these conditions are observed a complete separation of the colouring-matter of the blood is almost always effected, so that even on washing the precipitate with much water in the filter-press or in the filter-pump nothing returns into solution. The yellowish brown colouring-matter contained in the serum of some kinds of blood is not thrown down, but remains in the filtrate. Distinctly recognisable quantities of zinc are to be found in the filtrate only if compounds of organic acids were present in the blood. Otherwise mere traces of zinc exist as zinc albuminate, in smaller proportions the more the zinc powder is free from zinc oxide. As the deposit—a solid, reddish-brown, bulky mass,—retains no organic poisons except traces of hydrocyanic acid and carbon monoxide, we have in the filtrate all the glycosides, alkaloids, ptomaines, toxalbumens, enzymes, amides, &c.; in short, the examination of the filtrate is exclusively important for forensic chemistry. Concerning the solid residue we need merely remark that the hydrocyanic acid may be removed from it by extraction with alcohol and carbon monoxide by exhaustion in the air-pump.

The filtrate is incomparably more suitable than the original blood as well for the chemical as for the physiological detection of poisons. If its action upon animals is to be examined it is only requisite to shake up a portion with a drop of solution of sodium sulphide, and to filter off the precipitate of zinc sulphide. If the proportions are duly adjusted the liquid, free from zinc and sodium sulphide, can be injected subcutaneously into a mouse or into the circulatory system of a kitten. However, the filtrate can often be applied without the elimination of the zinc. The bacteria which swarm in putrid blood are almost entirely left behind in the residue. Where an absolute determination of bacteria is required the filtrate may be again passed through a Chamberland filter and thus the last residues of the germs may be removed. If the animal experimented upon exhibits grave phenomena of poisoning, a second portion of the original filtrate is mixed with a drop of solution of potassium ferrocyanide and a little acetic acid, the precipitate, which includes all the zinc and the albumenoids, is filtered, the filtrate is neutralised and injected into a second animal. If this animal, in contradistinction to the former, exhibits no phenomena of poisoning, the symptoms observed in the former subject must have been occasioned by an albumenoid poison, as in such dilute liquids other poisons are not precipitated by potassium ferrocyanide, or at most a portion of strychnine, which can be easily detected in the precipitate.

The isolation of the poisonous albumenoid substance can be undertaken only in the main portion of the original filtrate, either by treatment with alcohol in the ordinary manner or by "salting out" with ammonium sulphate. In those toxalbumens, however, which do not admit of the above mentioned methods of precipitation, e.g., those of venomous spiders, a more complete isolation of the poison is not yet practicable.

If the second experimental animal does not remain in health, but is taken ill like the first, we have a proof that the poison in question does not belong to the albumens, —at least not to those precipitable by ordinary means. The entire filtrate is then freed from albumen and the limpid filtrate is examined for other poisons by Dragendorff's method.—*Chemiker Zeitung*.

NEW METHOD FOR THE EXAMINATION OF FERROCYANIDES, FOR DETERMINING THE VALUE OF PRUSSIATE MELT, AND FOR ESTIMATING THE FERROCYANIDE IN SPENT LAMING'S MASS.

By R. ZALOZIECKI.

THE method is founded on the fact that the ferrocyanides in a solution of potassium or sodium ferrocyanide may be completely precipitated in the form of double ferrocyanides of zinc and alkali by an addition of zinc carbonate and the introduction of a current of carbonic acid gas. The equivalent quantity of potassium or sodium separated by the zinc from the ferrocyanides is transformed into the corresponding potassium or sodium carbonate, and the quantity of the ferrocyanide originally present may be found by an alkalimetric determination of the alkaline carbonate formed.

According to the experiments of the author, 3 mols. potassium ferrocyanide yield on decomposition 2 mols. zinc ferrocyanide, whilst 1 mol. potassium ferrocyanide remains undecomposed. The double salt therefore corresponds to the formula $2Zn_2FeCy_6 + K_4Cy_6$, and the decomposition is represented by the following equation—

$$3K_4FeCy_6 + 4ZnCO_3 = 2Zn_2FeCy_6 + K_4FeCy_6 + 4K_2CO_3.$$
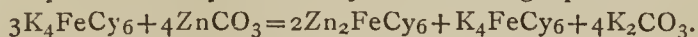
The reaction always takes place uniformly in heat, and even in the cold the transformation of potassium ferrocyanide is effected according to the above equation. A solution of sodium ferrocyanide behaves differently, since in the cold there is formed a double salt poorer in zinc, though in heat the same decomposition takes place as with potassium ferrocyanide. It is therefore always necessary to operate in heat.

The zinc carbonate to be used in the process is obtained by precipitating in heat a solution of zinc sulphate with sodium carbonate ; the basic carbonate thus obtained settles rapidly, and may be easily washed. It is convenient to weigh approximately whilst in the moist state the basic zinc carbonate obtained from a known quantity of zinc sulphate, and preserve it in a closed glass jar. The author generally uses in his experiments 20 grms. moist zinc carbonate, corresponding to 2·25 grms. zinc. Such an excess does not affect the results, but the decomposition may be produced completely by a much smaller quantity of zinc.

In a determination of ferrocyanide the solution of the salt is mixed in a small flask with a known quantity of zinc carbonate, and carbonic acid is passed into the heated solution for from half to one hour. The treatment with carbonic acid is continued until the original decided yellow colour of the solution has disappeared, or until the addition of a ferric salt to a portion of the clear liquid no longer gives a blue precipitate. When cold it is put into a measuring flask containing 250 c.c., filled up to the mark, and filtered through a dry filter into a dry flask, wherein 50 c.c. of the filtrate are titrated with sulphuric acid of known strength as indicator. According to the above equation the quantity of the ferrocyanide can be calculated from the potassium or sodium carbonate thus determined, as four equivalents of potassium or sodium carbonate represent three equivalents of ferrocyanide.

The author observed that the presence of large quantities of alkaline sulphates or chlorides lead to the formation of a compound richer in zinc. This effect is annulled if at the same time there is present an excess of alkaline carbonate. In examining the salts of prussiate melts the presence of sulphates must be taken into consideration, and in case the sulphates are present in considerable quantity a known excess of potassium or sodium carbonate must be added prior to the introduction of the zinc carbonate; otherwise the results will be too high.

For the examination of prussiate melts the author gives the following directions:—10 grms. of melt are dissolved in 100 c.c. of water, the volume of the insoluble residue being taken into consideration. In 25 c.c. of the solution the alkalinity is determined with normal acid and methyl orange: 50 c.c. of the solution are treated, as described above, with 10 grms. moist zinc carbonate, carbonic acid is introduced for half an hour into the hot solution, which when cold is placed in a 100 c.c. flask, and filled up to the mark; 50 c.c. of this solution are titrated with decinormal acid after the number of c.c. acid required for the alkalinity of the mark have been added.

If, in the determination of the alkalinity in the coloured solution of the melt, the change of colour is difficult to recognise, the solution can be exactly neutralised with dilute sulphuric acid, and, prior to the decomposition with zinc carbonate, 20 c.c. of a normal solution of potassium carbonate. There is no difficulty in titrating back, as the liquid is colourless after the decomposition. If the acid is so standardised that 1 c.c. corresponds to 0·001 grm. potassium carbonate, the c.c. of the acid consumed in neutralising the potassium carbonate formed, multiplied by 0·8, give the per cents of anhydrous potassium ferrocyanide, and if multiplied by 0·92 the percentage of hydrous ferrocyanide in the original melt.

Sulphocyanides, if present, do not affect the result. Potassium sulphide is indeed converted into zinc sulphide and potassium carbonate, but this decomposition has no effect, as the potassium sulphide present is included in the result on determining the total alkalinity with methyl orange as indicator.

The method is applicable also in determining the ferrocyanide in spent "mass" from the gas purifiers (Laming's mass).

Zaloziecki proceeds as follows:—20 grms. of the mass, in a state of fine division, are gently heated on the water-bath for fifteen minutes with 20 c.c. 10 per cent potassa lye and a little water in a 100 c.c. flask. When the entire quantity of the ferrocyanide present is thus dissolved it is let cool, and the flask is filled up to the mark: 50 c.c. of the clear solution (or, more correctly. 45 c.c. if measured with a burette, as 20 grms. of the mass take up a volume of 10 c.c.), corresponding to 10 grms. of the sample, are boiled in a 100 c.c. flask over an open fire until the ammonia is entirely expelled, and it is then accurately neutralised with dilute acid. To facilitate the neutralisation a few drops of solution of phenolphthalein may be added, and the acid dropped in from a burette until the red colour disappears. On neutralisation

the sulphur separates out and the liquid becomes turbid, but this does not interfere with the further determination. The expulsion of the ammonia may also be effected by the addition of milk of lime, and the lime may next be removed by the solution of potassa, which renders the liquid clear. The solution thus prepared, in which all the ferrocyanogen is combined with potsssium, cannot be at once submitted to treatment with zinc carbonate and carbonic acid, as potassium sulphate (or chloride) is present in quantity, and would interfere with the reaction. He therefore first adds to the solution 20 c.c. of normal potassium carbonate, and then undertakes the decomposition in the manner described above, adding 5 grms. moist zinc oxide, and then passing carbonic acid for half an hour through the hot solution. When the reaction is completed, and the liquid is cooled, the flask is filled up to the mark, and one-half of the liquid — representing 5 grms. of the mass — is titrated with decinormal acid and methyl orange. The quantity of normal acid equivalent to the normal potassium carbonate added (10 c.c.) is either added at the outset or deducted from the total sum of c.c. of acid consumed.

If the acid has been so standardised that 1 c.c. represents 0·001 grm. potassium carbonate, the c.c. of acid consumed in titrating back, if multiplied by the coefficient 0·46, will give the percentage of crystalline ferrocyanide existing in the purifying mass.—*Zeitschrift Analyt. Chem.,* vol. xxx., 484.

PROPERTIES OF PRECIPITATES, &c.

By E. WALLER, Ph.D.

ONE division of Fresenius's book on "Quantitative Analysis" treats of "forms," in which are given the properties of the various forms in which substances are separated for the purpose of weighing and determination.

If has seemed to the writer that those properties might be described in a manner more convenient for reference, and also that there might be added the properties of various precipitates, &c., which are used in analytical work for purposes of *separation*. Of course only those properties are considered which have a bearing on the usual manipulation of the different substances. For convenience the information has been grouped under the heads—

"*Remarks*" (*Rem.*), giving points not properly belonging under any of the succeeding heads.

Conditions (*Cond.*), referring to the character of the solutions in which the separation can be made.

Solubilities (*Sol.*), under which the influences of different solvents which may be used in ordinary work are considered.*

Contaminants (*Contam.*), which is restricted to those substances only which would not be expected to precipitate if alone under the conditions obtained.

Ignition (*Ign.*), or the behaviour of the compounds designated on heating to a high heat in the way usually pursued with most of them. Under this head it is also necessary to consider the effect of ignition in contact with filter paper or other carbonaceous substances indicated for brevity as "C."

A Table is given which is intended to indicate at a glance the precipitates, &c., used, and the forms in which they are weighed in case that is the object in view. Of course the forms designated as for *weighing* can also be used for purposes of *separation*.

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* The terms "soluble" and "insoluble," as used in text-books of analytical chemistry, are usually misunderstood by students. The terms are used in a relative—not in an absolute—sense, *e.g.*, when a precipitate is said to be "insoluble," the meaning usually is that under ordinary conditions of work, with a moderate bulk of solution, &c., the degree of solubility is so small that no material error is involved by regarding the separation as complete.

Element, &c.	Purpose.	Obtained, or precipitated as—	Prepared for weighing by—	Weighed as—
NH_4	Weighing.	$(NH_4)_2PtCl_6$.	Drying or ignition.	$(NH_4)_2PtCl_6$ or Pt.
K	,,	K_2PtCl_6.	,, ,,	K_2PtCl_6 or Pt.
	,,	KCl.	Ignition.	KCl.
	,,	K_2SO_4.	,,	K_2SO_4.
Na	,,	NaCl.	,,	NaCl.
	,,	Na_2SO_4.	,,	Na_2SO_4.
Ca	,,	CaC_2O_4.	{ ,, ,, ,,	$CaSO_4$. $CaCO_3$. CaO.
	Separation.	$CaCO_3$.		
Mg	Weighing.	$MgNH_4PO_4$.	,,	$Mg_2P_2O_7$.
	Separation.	$Mg(OH)_2$.		
Ba	Weighing.	$BaSO_4$.	,,	$BaSO_4$.
	Separation.	$BaCO_3$.		
Fe	Weighing.	$Fe_2(OH)_6$.	,,	Fe_2O_3.
	Separation.	$Fe(OH)n(C_2H_3O_2)_{6-n}$.		
Al	Weighing.	$Al_2(OH)_6$.	,,	Al_2O_3.
	,,	$Al_2(PO_4)_2$.	,,	$Al_2(PO_4)_2$.
	Separation.	$Al_2(OH)n(C_2H_3O_2)_{6-n}$.		
Cr	Weighing.	$Cr_2(OH)_6$.	,,	Cr_2O_3.
Ti	,,	H_2TiO_3.	,,	TiO_2.
	Separation.	Na_2TiO_3.		
Zn	Weighing.	$2ZnCO_3 3Zn(OH)_2$.	,,	ZnO.
	,,	$ZnNH_4PO_4$.	,, or drying.	$Zn_2P_2O_7$ or $ZnNH_4PO_4$.
	Separation.	$ZnS.H_2O$.		
Mn	Weighing.	$2MnCO_3H_2O$.	Ignition.	Mn_3O_4.
	,,	$MnNH_4PO_4$.	,,	$Mn_2P_2O_7$.
	Separation.	MnO_2.		
Ni	Weighing.	Ni (electro).	Drying.	Ni.
	,,	$Ni(OH)_2$.	} Ignition.	NiO.
	,,	$Ni_2(OH)_6$.		
	Separation.	$NiS.H_2O$.		
Co	Weighing.	$6KNO_2.Co_2(NO_2)_6$.	Ignition.	$3K_2SO_4+2CoSO_4$.
	Separation.	$CoS.H_2O$.		
Cu	Weighing.	Cu (electro).	Drying.	Cu.
	,,	$Cu(OH)_2$.	Ignition.	CuO.
	,,	CuS.	,,	Cu_2S.
Pb	,,	$PbSO_4$.	,,	$PbSO_4$.
	,,	$PbCrO_4$.	Drying.	
	Separation.	PbS.		
Ag	Weighing.	AgCl.	Ignition.	AgCl.
As	,,	As_2S_3.	Drying.	As_2S_3.
	,,	$MgNH_4AsO_4$.	Ignition.	$Mg_2As_2O_7$.
Sb	,,	Sb_2S_3.	,, or drying.	Sb_2O_4 or Sb_2S_3.
Sn	,,	$H_{10}Sn_5O_{15}$.	,,	SnO_2.
		SnS_2.		
$S.SO_2 S_2O_3 SO_3$, &c...	,,	$BaSO_4$.	,,	$BaSO_4$.
P, P_2O_5, &c.	,,	$MgNH_4PO_4$.	,,	$Mg_2P_2O_7$.
	Separation.	$12MoO_3(NH_4)_3PO_4+$		
C, CO_2, &c..	Weighing.	{ Na_2CO_3, K_2CO_3, &c., or $Na_2CO_3+CaCO_3BaCO_3$. }	Absorption.	{ Na_2CO_3, K_2CO_3, &c., or $Na_2.CO_3+CaCO_3BaSO_4$. }
Si and SiO_2	,,	xH_2OSiO_2.	Ignition.	SiO_2.
Cl	,,	AgCl.	,,	AgCl.
N and HNO_3	Measuring.	N or NO.		
	Titration.	NH_3.		
	Weighing.	$(NH_4)_2PtCl_6$.		$(NH_4)PtCl_6$ or Pt.

$(NH_4)_2PtCl_6$.

Rem.—Precipitant, $PtCl_4$.

Yellow, perceptibly crystalline if formed slowly. Sometimes it is dissolved from the paper by hot water into a weighed capsule, and the solution evaporated, thus avoiding the uncertainties involved in the use of weighed filters.

Cond.—Solution should contain only chlorides. Sodium salts only permissible. Solution should be cold, slightly acid, consisting chiefly of strong alcohol; an excess of $PtCl_4$ should be present.

Sol.—Somewhat soluble in cold, more so in hot, water. Fairly insoluble in strong alcohol, though more soluble than the corresponding potassium compound. Solubility in alcohol diminished by addition of ether. Its solubility also increases more rapidly by a rise in temperature or the dilution of the alcohol. Solubility increased by acid (HCl) or by alkali, diminished by $PtCl_4$ or Na_2PtCl_6.

Contam.—NaCl, which is not very soluble in alcohol. If sufficient $PtCl_4$ has been added to form Na_2PtCl_6, the amount of contamination is small. The Na_2PtCl_6 crystals are more strongly coloured and different in shape (needle shaped), so that they can be readily detected. Can be removed by a short digestion with cold alcohol.

Ign.—Decomposed, leaving spongy platinum. Unless the heat is slowly raised some Pt may be volatilised with the products of decomposition.

KCl.

Rem.—Obtained by evaporation of the solution and gentle ignition. Frequently, when in admixture with NaCl, the sum of the chlorides is thus obtained, and the KCl determined by $PtCl_4$, the NaCl calculated, or the chlorine is determined and the proportions calculated. Salts containing K combined with acids capable of expulsion by HCl, may be evaporated with excess of HCl.

Cond.—Solution should contain only chloride or salt convertible into chloride by evaporation with HCl. Ammonia salts and such others as may be expelled by evaporation and gentle ignition may be present.

Sol.—Soluble in water, less so in alcohol or strong HCl.

Contam.—NaCl, see under remarks. If the solution has been long exposed to the air of the laboratory, it usually contains some organic dust, which carbonises by ignition, requiring filtering and re-evaporation.

Ign.—Decrepitates somewhat unless dried for some time. Fuses at a low red heat, and volatilises at temperatures a little higher, a small amount of caustic alkali being usually formed at the same time.

K_2SO_4.

Rem.—Obtained by evaporation of the solution, or by adding H_2SO_4 to solutions containing combinations with volatile acids (chloride, nitrate, acetate, &c.), evaporating, and igniting. In cases of admixture with Na salts, processes similar to those indicated under KCl may be used.

Cond.—Salts forming non-volatile sulphates, or containing non-volatile acids (H_3PO_4, &c.) should be absent.

Sol.—Moderately soluble in water; much less so in alcohol.

Contam.—Na_2SO_4 or other non-volatile sulphates.

Ign.—Practically non-volatile in the heat of an ordinary Bunsen burner if the heat is not unnecessarily prolonged. Where the solution has contained an excess of H_2SO_4, some undecomposed $KHSO_4$ always remains, which can be best decomposed, or converted into K_2SO_4 by heating with a few lumps of solid ammonium carbonate. Ignited with C, K_2S may be formed. The conditions usually obtained, however, do not afford this result.

(To be continued.)

Modification of the Spectroscope.—P. Schottländer (*Zeit. fur Instrum. Kunde*).—The object is to determine the coefficients of extinction of absorbent bodies.

NOTICES OF BOOKS.

A Theoretical and Practical Treatise on the Manufacture of Sulphuric Acid and Alkali with the Collateral Branches. By GEORGE LUNGE, Ph.D., Professor of Technical Chemistry at the Federal Polytechnic School, Zurich (formerly Manager of the Tyne Alkali Works, South Shields). Second Edition, Revised and Enlarged. Vol. I.—Sulphuric Acid. London: Gurney and Jackson. 8vo., pp. 940.

(SECOND NOTICE.)

THE author naturally does not overlook the nuisance arising from the escape of sulphurous acid, but he reminds his readers that chemical works are not the sole offenders in this respect, as this acid occurs in very large quantity in all coal smoke, and that the most perfect smoke combustion cannot do away with this. He shows that the vapours escaping from the high chimney shafts of factories are less hurtful than those from brick-kilns, coke-ovens, &c.

Metallic sulphides other than pure pyrites are often not good materials for the manufacture of sulphuric acid. According to Bode an admixture of 18—20 per cent of galena renders pyrites unfit for burning. The manufacture of nitric acid is fully described, with figures showing proposed modifications of the apparatus.

It is remarked that some manufacturers substitute for a part of the nitre used the waste acid from the production of nitrobenzene, nitroglycerin, &c. The author gives the caution that in this case all drops of oily matter must be carefully excluded.

When speaking of the injurious action of sulphur dioxide on animal and vegetable life the author notes some prevailing errors. Hirt has stated that 1—3 per cent SO_2 may be breathed without danger to health. Ogata, on the contrary (*Archiv. fur Hygiene*), as here quoted, found experimentally that 0·04 per cent SO_2 causes difficulty of breathing in a few hours, and that he could not take a single full breath in air containing 0·05 per cent SO_2. But the influence of acid vapours upon cattle, trees, and even upon the soil, has been grossly exaggerated.

The bleaching-action of sulphurous acid has not, according to the author, been fully explained.

The occurrence of free sulphuric acid in certain animal secretions is mentioned as a curious fact. The saliva of *Dolium galea* contains 2·47 per cent sulphuric acid and 0·4 per cent hydrochloric acid both in the free state.

Whilst speaking of the specific gravity of "rectified oil of vitriol," called O.V., or sometimes D.O.V., the author refers to the inaccuracy of ordinary hydrometers. He remarks, however, "Still, it must be conceded that in England at least there is a possibility of making the hydrometers all alike, the basis of Twaddell's system being a plain and unmistakeable one, as every degree is equal to a difference of 0·005. But matters are far worse on the Continent and in America, where Baumé's hydrometer is almost universally used. Unfortunately the degrees of this instrument, as stated by various authorities, answer to very different specific gravities, and those of the instruments found in trade often show even far greater deviations." The rational hydrometer on Baumé's system is graduated according to the formula—

$$d = \frac{144·3}{144·3 - n,}$$

where d stands for any given specific gravity, and n for the degree Baumé corresponding. Another modification devised by Gerlach is also sometimes used on the Continent, whilst American manufacturers have adopted a third scale. If a liquid is found to mark 66° B., its specific gravity may, according to the scale adopted, be 1·842, 1·817, or 1·835 !

As regards the specific gravities of mixtures of sulphuric

acid and water, the author uses the values determined last year by himself and Isler. For those of Bineau and Kolb the reader is referred to the former edition. Those of Ure and Dalton, and still more the tables of Vauquelin and D'Arcet, which, though totally incorrect, are still used in the south of France, are not quoted.

The experiments here given bearing on the behaviour of different mixtures of cast-iron with sulphuric acid are of great importance. The different qualities of cast-iron are equally resistant against acid of 168° Tw. and against weaker acids at 20° and 100°. Scotch pig and mixtures in which it is present are most attacked.

Both cast- and wrought-iron resist monohydrated sulphuric acid better than copper or lead.

The behaviour of lead, pure and alloyed, with sulphuric acid, is still open to doubt. The author's own experiments given in the appendix (p. 892) show that pure, soft lead is less attacked than the so-called "hard lead" containing 1·8 per cent of antimony. Glover (CHEMICAL NEWS, vol. xlv., p. 105) obtained corresponding results, whilst Calvert and Johnson, and subsequently Mallard and Hasenclever, find that lead is all the more acted upon the purer it is.

The section on the behaviour of sulphurous and sulphuric acid with the nitrogen oxides is very elaborate and of thorough practical value.

As a standard acid the author recommends hydrochloric acid. Oxalic acid, though extensively used, has, he considers, great drawbacks. It is extremely difficult to prepare in the pure and dry state without losing some of its crystalline water ; it does not keep in weak solutions, and it cannot be employed with methyl orange, which he prefers as an indicator.

Among the impurities encountered in sulphuric acid a prominent place is of course due to arsenic. Here Selmi is quoted for the statement that arsenic may be detected in acid, which does not react with the Marsh test by diluting 1000 grms. of the sample with 300 grms. of water, adding some lead chloride, distilling and testing the first portions of the distillate with sulphuretted hydrogen.

For the analysis of nitrous vitriol the author uses a special modification of the permanganate process. The estimation of nitrous acid by means of aniline, which is converted into a diazobenzol salt, the end of the reaction being shown by potassium iodide. It offers no advantages as compared with the permanganate process, which is simpler.

For determining the total nitrogen acids in sulphuric acid the author recommends Walter Crum's process, for which he has constructed a special instrument, the "nitrometer," which is here figured. Since the publication of his paper, Campbell, Davis, and possibly others have all designed nitrometers which the author, however, considers less satisfactory than his own instrument. As the nitrometer, however, requires reference to certain tables, he has constructed another instrument, the gas-volumeter, which dispenses with the use of tables.

With chapter 4 the author enters upon the actual manufacture of sulphuric acid. He describes and figures in the first place the burners for brimstone now, of course, comparatively little used. Next follow the appliances for burning pyrites, beginning with the ore-breaker of Blake, as improved by Broadbent and Son, of Stalybridge, and those of Motte, Durand, and Chaptal Vapart, &c.

The pyrites-burners for lumps are exhaustively treated of, followed by the kilns for smalls. The original plan of working up smalls with clay into the form of balls involves so much inconvenience that it has been abandoned almost everywhere in favour of the shelf-kilns of Malêtra, Schaffner, and others.

The various attempts to construct chambers of materials other than lead, or to dispense with them altogether, have proved unsuccessful. Their construction, arrangement, and dimensions are made the subject of elaborate consideration.

As regards the supply of nitric acid to the chambers, there is a choice between the introduction of solid nitre, as most usual in Britain, of liquid acid, preferably running it along with the nitrous vitriol through the Glover tower, and of an aqueous solution of nitrate.

The respective advantages of the solid and the liquid form are fully weighed. Dr. Lunge's decision is distinctly in favour of the use of liquid acid.

Passing over the carefully written sections on the supply of steam and of air we come to the question of the optimum strength of chamber acid. In England strengths of 120°—130° Tw. are adhered to, whilst on the Continent 113° Tw. is rarely exceeded, and in America 112°—116°. The author awards the preference to the weaker acid.

The experiments of H. A. Smith ("Chemistry of the Sulphuric Acid Manufacture") are pronounced quite unsatisfactory. As regards the Glover tower the author's conclusion, drawn from the observation of many of the best alkali works—English, French, and German,—is distinctly favourable. So far from wasting nitre it has reduced the consumption of nitre and "forms an essential part of every well-arranged sulphuric acid works."

The drawbacks of the Glover tower are contamination of the acid with iron and alumina. Hence it cannot well be concentrated in platinum vessels.

Anent the formation of sulphuric acid the author discusses the theories of Clement and Désormes, of Davy, Berzelius, Peligot, R. Weber, Winkler, Raschig, and the author's own.

But we must here somewhat abruptly close our examination of this excellent work. Were we to notice every point which well deserves it we should fill a fair-sized volume. Dr. Lunge shows himself *facile princeps* among experts on the manufacture of sulphuric acid and its accessories, at once a thorough practician and a scientific theorist.

CORRESPONDENCE.

THE CHEMISTS' BENEVOLENT FUND.

To the Editor of the Chemical News.

SIR,—Every one of your readers will be glad to know that the challenge sent to the CHEMICAL NEWS early in the year, as to £50 being forthcoming to start a Chemists' Benevolent Fund if nineteen similar or larger subscriptions were offered, has been taken up so satisfactorily that these twenty donations alone amount to £1550. Moreover, other fifties are expected.

Further, promises of sums varying from £2 to £25 amount to £600. These donations, £2150, invested to pay 4 per cent, would yield £86 annually. But promises of annual subscriptions also have been received, varying from 1 to 5 guineas a year, and amounting to £108. Therefore the already promised annual income is £194, representing a capital of £4850.

As a consequence of your kind publication of this letter I shall hope to receive promises of a few more pounds a year or a few more hundreds of capital. So that the net result of the effort to establish this fund within the Jubilee year of the Chemical Society is, say, reckoned as Capital, £5000 ; reckoned as Annual Income, £200.

Comparing these results with those disclosed by the histories of the benevolent funds of other professional bodies, and bearing in mind the not very large number of the followers of chemistry in Great Britain, it will be obvious that we have made a most satisfactory start in the founding of a Chemists' Benevolent Fund. In short, the project, not altogether a new one, has been received with distinct enthusiasm.

The success so far is due, first, to the generous example set by Mr. Mond, Dr. Gladstone, and others ; secondly, to the practical and popular suggestion in March last by the

then President of the Chemical Society, that any such fund should be administered by a representative outside Committee nominated by the Council of the Chemical Society; thirdly, to the support at once accorded by the present Presidents of the four chief Societies of British chemists, namely, the Chemical Society, the Institute of Chemistry, the Society of Chemical Industry, and the Society of Public Analysts. Fifthly, to the fact that in the first circular broadly issued on the subject eighty-six of the 101 officers and members of the Councils of the four Societies just mentioned had already allowed their names to be put forward as supporters of the fund.

Very few refusals of support have been received. No one opposes the scheme. The lines of organisation mentioned in the circular are approved. Two or three theoretical objections have been mentioned, and definitions and details have in a few cases been desired. But only small difficulties incident to the birth and growth of all such funds have been or are likely to be encountered.

Judging by experience it will only be necessary for chemists to apply to wealthy friends interested in chemistry, for consulting chemists to approach industrial clients who have been enriched by chemistry, and for a powerful Committee to appeal to the great brewing, gas-making, water-supplying, and other companies, firms, and corporations whose organisations are closely connected with our science, for the foregoing amount of capital or income to be doubled. The fund might then be left to the growth usual to such funds, if, indeed, any encouragement of further growth should be necessary.

The undersigned would be glad to receive further promises of donations or annual subscriptions within the next ten days, after which the whole matter will be laid before the Council of the Chemical Society.—I am, &c.,

JOHN ATTFIELD.

Watford, Herts; or 17, Bloomsbury Square, W.C.
October 22, 1891.

BEHAVIOUR OF BUTYRIC ACID WITH ALKALINE PERMANGANATE.

To the Editor of the Chemical News.

SIR,—Will you allow me to assure Mr. Johnstone and your readers that in furnishing an analytical journal with an abstract of C. Mangold's paper "On the Estimation of Glycerol" (*Zeit. fur Angew. Chemie*, 1891, p. 401), nothing was further from my intention than to give a one-sided report or to suppress facts which might in any way have furnished corroboration of Mr. Johnstone's assertion that butyric acid when boiled with alkaline permanganate yields oxalic acid in more or less quantitative proportions. I have no interest of any kind beyond a strictly scientific one in the matter, and would experience nothing but pleasure if other observers did agree with Mr. Johnstone, although personally I had not been able to arrive at the same results as he did.

From Mr. Johnstone's remarks I cannot but conclude that he is either but imperfectly acquainted with the German language, or that he has not seen Mangold's original paper. I therefore give a literal translation of Mangold's words as far as they touch this matter.

" The presence of butyric acid does not influence the results in any way, as the following experiments show, butyric acid not being oxidised at all by permanganate in alkaline solution in the cold. On continued boiling of butyric acid with excess of alkali and permanganate it yields, *as shown by Johnstone* (CHEMICAL NEWS, vol. lxiii., p. 111), abundant quantities of oxalic acid. But I have satisfied myself by repeated experiments that by following the original method of Benedikt and Zsigmondy the amount of oxalic acid is either not increased at all in the presence of butyric acid or only very slightly, traces at most of butyric acid being attacked under these conditions of temperature and concentration.

" The satisfactory agreement of the whole of the results is seen from the following table :—

				Glycerin p.c.
1. From the specific gravity				96·0
2. Herbig-Mangold method, without heating				96·58
3. ,, ,, ,, ,,				96·11
4. Herbig-Mangold method, with heating ..				95·95
5. ,, ,, ,, ,,				95·64
6. ,, ,, ,, ,,				95·29
7. In presence of 90 butyric acid to 100 glycerin				95·95
8. ,, ,, ,, ,,				96·20."

Clearly, therefore, Mangold does not corroborate Mr. Johnstone. The statement that butyric acid yields oxalic acid is evidently made by Mangold upon Mr. Johnstone's authority, and is not confirmed, but, on the contrary, disproved by Mangold's own observations.

Mangold's analytical figures all agree with each other as nearly as estimations of glycerin by the oxalate method can be expected to agree, and I am sure that the readers of the CHEMICAL NEWS, and perhaps Mr. Johnstone, will see that, if " carefully suppressed " by me, they were at all events not suppressed to Mr. Johnstone's disadvantage.—I am, &c.,

OTTO HEHNER.

11, Billiter Square, London,
October 20, 1891.

THE RELATION BETWEEN THE CHEMICAL CONSTITUTION OF CERTAIN ORGANIC COMPOUNDS AND THEIR ACTION UPON THE ULTRA-VIOLET RAYS.

To the Editor of the Chemical News.

SIR,—My attention has been directed to Prof. Dunstan's letter in your issue of July 3rd, 1891, p. 10. I trust that it is not too late to express my regret that he should have considered it necessary to write. Any one who carefully reads my letter of June 5th, p. 309, will observe that I did not suggest that Prof. Dunstan was responsible for the misunderstanding which has arisen with reference to the account of his lecture which appeared in the *Pharm. Journal*, xi , p. 54, 1881. My thanks are due to Prof. Dunstan for having undertaken to send a correction to the *Zeit. fur Phys. Chemie*, and also may I add for drawing attention to the fact that the following misleading notice appears in the British Association Report, 1881, " On our Knowledge of Spectrum Analysis " :—

> CHEMICAL RELATIONS, 1880.—" The Relation between the Chemical Constitution of Certain Organic Compounds and their Action upon the Ultra-Violet Rays " (July 8).—W. R. Dunstan, *Pharm. J. Trans.*, [3] xi., 54—56.

This Report was drawn up with extraordinary care; for example, when it could be ascertained that a paper was read some time before it appeared in print the date of reading as well as its publication in type was noted. It is perfectly evident that the compiler of the list of works in the Report was misled. I must cry *Peccavi* to being one of fifteen on the committee. I believe that the circumstances which gave this lecture the prominence of an original paper were purely accidental.—I am, &c.,

W. N. HARTLEY.

36, Waterloo Road, Dublin.
Oct. 12, 1891.

Contamination of Alkaline Polycarbonates by Heavy Metals, especially Zinc.—Nicolas Huss.—If such carbonates are preserved in metal vessels, the latter are attacked with escape of hydrogen and formation of metallic carbonates. The ammoniacal salts act more strongly than the corresponding potassium and sodium salts. Besides zinc, iron and magnesium are attacked, whilst manganese, chromium, cobalt, nickel, lead, arsenic, &c., are scarcely attacked.—*Zeit. Anal. Chemie.*

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxiii., No. 14, October 5, 1891.

On the Simultaneous Existence in Cultures of Staphylococcus of a Vaccinating Substance Precipitable by Alcohol, and of a Predisposing Substance Soluble in Alcohol. — A. Rodet and J. Courmont.—The nature of this communication is sufficiently shown by the title.

Zeitschrift für Analytische Chemie.
Vol. xxx., Part 3.

A New Modification of the Dalton-Pettenkofer Method of Determining Carbonic Acid in the Air.—Arsenius Lebedinzeff.—This memoir cannot be reproduced without the seven accompanying figures.

Qualitative and Quantitative Demonstration of Iodides in Urine.—Dr. Adolf F. Jolles.—(a) *Qualitative Detection.* — About 10 c.c. urine are mixed with an equal volume of strong hydrochloric acid, and 2 or 3 drops of a weak solution of chlorine are then added with a pipette in such a manner that they may run down along the inner side of the test-glass. In presence even of very trifling quantities of iodine, there appears at the surface of contact of the two liquids a yellowish-brown ring, which becomes of an intense blue after the addition of a solution of starch. It is known that the presence of indican is shown in the same manner. Still, the presence of indican in whatever quantity cannot mask the above reaction, since the iodine ring has a much more intense colour and appears higher than and separate from the indican ring. The addition of an excess of chlorine is to be avoided. (b) *Quantitative Determination.*—50 c.c. of the urine are evaporated down and the residue carbonised over a Bunsen burner (incineration is not necessary). The carbon is lixiviated with hot water, a solution of silver nitrate is added, and the liquid is acidulated with dilute nitric acid. It is not necessary to add silver nitrate until no further precipitate is formed, since silver chloride is thrown down only when all iodine has been thrown down, and the proportion of chlorine in the urine has no relevance to the method. The precipitate of silver chloride and iodide is filtered off, washed with water containing nitric acid, dried, gently heated in a crucible to fusion, let cool, and weighed. The separation of the silver iodide from the silver chloride is effected after the indirect determination. For this purpose a portion of the mixture is placed in a porcelain boat previously heated and weighed. It is now weighed along with its contents, which are heated to fusion and exposed to a current of chlorine gas in order to convert the silver iodide into chloride. It is let cool in the current of chlorine and the boat is weighed. If there is a loss of weight, Dg, the quantity I of the iodine is found as follows :—For 127 parts of iodine the loss of weight would be 91·5 (I − Cl = 127 − 35·5 = 91·5). Consequently we may conclude inversely that if we find a difference of 91·5, 127 parts of iodine were originally present. But since the difference was not 91·5, but D, it is plain that $I = \dfrac{127D}{91·5}$.

A New Process for Examining Butters and Fats.—J. König and F. Hart.—This memoir will be inserted at some length.

Belgian Method for Determining the Soluble Phosphoric Acid (*i.e.*, in Water) **in Superphosphates.**—D. Crispo.—This paper will be inserted in full.

Arrangement for Weighing Oils.—Carl Mangold.—The author gives a figure of a convenient apparatus for this purpose.

On Indicators.—Dr. Otto Foerster.—The author gives the address of a Berlin firm who supply lacmoid of satisfactory quality. He uses as indicator a solution of 3 grms. lacmoid purified by his method, and 5 grms. of Casella and Co.'s naphthol green, in a mixture of 700 c.c. water and 300 c.c. alcohol. Unlike malachite green naphthol green does not precipitate lacmoid, and when mixed in the above proportions it produces a very pure blue in neutral and alkaline liquids, whilst it colours acid liquids an onion peel red.

The Bacteriological Examination of Waters.—Dr. G. Frank.—Already inserted.

The Use of Dry Reactions in Qualitative Analysis.—W. Tate.—(From the CHEMICAL NEWS).

The Influence of Inactive Bodies upon the Rotatory Power of Active Substances.—A number of notices by Gernez (*Comptes Rendus*), Haller (*Comptes Rendus*), Farnstoiner (*Berichte Deutsch. Chem. Gesell.*), Bremer (*Recueil de Travaux Chimique des Pays Bas*), and Bribram (*Monath's Hefte für Chemie*).

Attraction for Precipitates of Places on the Sides of Beakers which have been Rubbed with the Stirring-Rod. — G. Watson. — From the CHEMICAL NEWS.

Cause of Band- and Line-Spectra.—H. Kayser (*Annalen der Physik*).—No details are given.

Photography of the Spectra of Metals.—V. Schumann.—(From the CHEMICAL NEWS).

The Absorption-Spectra of the Solutions of Iodine in Different Liquids.—H. Rigollot (*Comptes Rendus*).

Colours of the Solutions of Iodine.—H. Gautier and G. Charpy (*Comptes Rendus*).

Connection of the Solubility of Glass with its Composition.—References to several papers in the *Zeit. für Instrum. Kunde, Chemische Industrie*, and *Thon Industrie Zeitung*.

Araeometer for Complete Submersion.—N. Reggiani (*Atti dei Lincei*).—Already inserted.

Determining the Specific Gravity of Solids.—G. H. Failyer.—(From the *Journal of Analytical Chemistry*).

A New Automatic Mercurial Air-Pump.—Max Stuhl (*Ber. Deut. Chem. Gesell.*).—This paper requires the accompanying cut.

Intermittent Mercurial Air-Pump.—K. Prytz (*Ann. der Physik*).—Already inserted.

A New Exploding Furnace.—Couvant and Moscheles (*Chemiker Zeitung*).—The construction of the apparatus cannot be made intelligible without the accompanying cut.

Apparatus for Heating Substances under Pressure.—A. Pfungst (*Chem. Zeit.*), and Hugo Schiff (*ibid.*), where also the illustration is essential. Tubes for exposing substances to high temperatures in currents of gases have been devised by H. N. Warren (CHEMICAL NEWS) and A. Richardson (*ibid*).

Reading Off Burettes.—G. Kottmayer (*Pharm. Post*). —This paper requires the three accompanying cuts.

Capsule-Holder.—P. Boessneck (*Chem. Zeit.*).—An artificial hand for lifting hot evaporating basins, &c.

Self-Acting Apparatus for Shutting-off Gas-Flames. — J. Hartkorn (*Chemiker Zeitung*). — Already inserted.

Apparatus for Determining Melting-Points of Fats.—Muter.—(From the *Analyst*).

Constants of Ammonia.—Hans von Strombeck.—(From the *Proceedings of the Chemical Section of the Franklin Institute*).

Detection of Impurities in Mercury.—G. Gore.—(From the CHEMICAL NEWS).

Quantitative Determination of Pyridine Bases in Ammonia.—W. Kinzel (*Pharm. Central Halle*).—Already inserted.

Preparation of Gaseous and Aqueous Hydrobromic Acid.—Notices of papers by A. Recoura (*Comptes Rendus*) Alex. Naumann (*Chemiker Zeitung* and *Ber. Deut. Chem. Gesell.*), Stahlschmidt (*Apotheker Zeitung*), Willgerodt (*Chemiker Zeitung*), and Feit and Kubierschky (*ibid.*).

On α-Naphthol Benzeïn as Indicator.—R. Zaloziecki (*Chemiker Zeitung*).—Already inserted.

A New Method for Opening up Silicates.—P. Jannasch (*Ber. Deutsch. Chem. Gesell.*).—This paper requires the accompanying illustration.

Determination of the Final Point in the Titration of Zinc by means of Potassium Ferrocyanide in an Ammoniacal Solution. — Fernando Moldenhauer (*Chemiker Zeitung*).—This memoir will be inserted in full.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Bleaching Powder.—Can any of your correspondents let me know the amount of the total annual production of bleaching powder in Great Britain ?—ALFRED MILNES.

Thermo-Chemistry.—I notice under "Notes and Queries" (vol. lxiv., p. 153) an enquiry for recent and valuable works on thermochemistry. Although I have examined the works in the German language, I believe the last two are translations from the English. As far as I remember I give details:—Horstmann, "Theoretische Chemie u. Thermo-chemie," 1885 ; price, 13 marks. Naumann, "Lehr- und Hand-buch der Thermo-chemie ; " price, 15 marks. Thomsen, "Thermo-chemische Untersuchungen ; " price, 51 marks ; 4 volumes. These books can be obtained from Meyer and Müller, Berlin, W., Markgrafenstr. No. 51, from whose catalogue I have copied the titles.—S. B.

THE CHEMICAL NEWS.

Vol. LXIV., No. 1666.

A NEW LABORATORY PROCESS FOR PREPARING HYDROBROMIC ACID.

By G. S. NEWTH.

THIS method is a synthetical one, and consists in passing a stream of hydrogen and bromine vapour over a spiral of platinum wire heated to bright redness by means of an electric current. A glass tube, about 7 inches long and 5-8ths of an inch bore, is fitted at each end with a cork carrying a short straight piece of small tube; through each cork is also fixed a stout wire, and these two wires are joined by means of a short spiral of platinum wire, the spiral being about 1 inch long. One end of this apparatus is connected to a small wash-bottle containing bromine, through which a stream of hydrogen can be bubbled. The other end is attached to a tube dipping into a vessel of water for the absorption of the gas, or, if a large quantity of the solution is required, to a series of Woulf's bottles containing water. Hydrogen is first slowly passed through the tube until the air is displaced, when the platinum spiral is heated to bright redness by the passage of a suitable electric current. Complete combination takes place in contact with the hot wire, and the colour imparted to the ingoing gases by the bromine vapour is entirely removed, and the contents of the tube beyond the platinum are perfectly colourless. The vessel containing the bromine may be heated to a temperature of about 60° C. in a water-bath, at which temperature the hydrogen will be mixed with nearly the requisite amount of bromine to combine with the whole of it. So long as even a slight excess of hydrogen is passing, which is readily seen by the escape of bubbles through the water in the absorbing vessels, the issuing hydrobromic acid will remain perfectly colourless, and therefore free from bromine; so that it is not necessary to adopt any of the usual methods for scrubbing the gas through vessels containing phosphorus. When the operation is proceeding very rapidly a lambent flame occasionally appears in the tube just before the platinum wire, but this flame is never propagated back through the narrow tube into the bromine bottle. The precaution may be taken, however, of plugging this narrow tube with a little glass wool, which renders any inconvenience from this cause quite impossible. By this method a large quantity of bromine may be rapidly converted into hydrobromic acid without any loss of bromine, and the operation when once started can be allowed to proceed without any further attention.

COMMENTS ON MR. ROSS'S PAPER ON THE ORIGIN OF PETROLEUM.*

By BOVERTON REDWOOD.

MR. ROSS states that the theories of the origin of petroleum are all founded on some hypothetical process which differs from any with which we are acquainted. In illustration of this statement he asserts that the decomposition of fish could not produce "oil containing paraffin," and he characterises as erroneous the inference that petroleum was formed from the animal matter formerly contained in the fossil shells found in limestone. Presumably he is unaware that many years ago Warren and

* A reproduction of the remarks made by Mr. Redwood when the Paper in question was read before the British Association, Cardiff Meeting, 1891, Section G.

Storer, in the United States, obtained by the distillation of a lime-soap prepared from fish-oil a series of hydrocarbons identical with those contained in Pennsylvanian petroleum, and that more recently Engler, and afterwards Engler and Seidner—produced, by the distillation of fish-oil (Menhaden oil, chiefly triolein) and synthetical triolein, under a pressure of several atmospheres, a quantity of artificial petroleum. In his earlier experiments Engler isolated pentane, hexane, and heptane from the distillate, and in the later experiments conducted in association with Seidner, on a fairly large scale, several higher members of the paraffin series were separated, as well as olefines. During the distillation a considerable quantity of permanent gas, largely composed of methane, was evolved. The artificial petroleum, which was described as a nearly colourless fluorescent liquid, apparently resembling ordinary American kerosene in physical characters, was not only examined chemically, but was obtained in sufficient quantity to admit of its being practically tested by burning in lamps in comparison with the Pennsylvanian petroleum oil of commerce, and its illuminating power in two well-known German lamps was found to be high in relation to the consumption of oil.

It is worthy of note that Mr. Peckham, after a careful examination of the various "chemical" theories expressed in relation to them much the same opinion as that held by Mr. Ross in relation to all other theories than his own, viz., that they required the assumption of operations nowhere witnessed in Nature or known to Technology. In this connexion it would be interesting to know what direct experimental proof Mr. Ross has obtained of the correctness of his views. Mr. Peckham further pointed out, as objections to an inorganic theory, that it would not be expected that a process yielding a diversity of products, under slightly varying circumstances, would furnish a uniform result over a very wide area, or that the same process acting upon similar materials would produce the very different varieties of petroleum met with. Thus samples of Pennsylvanian petroleum of the same density obtained from widely separated localities furnish identical results upon analysis, and the same may be said of Californian petroleum; yet the two descriptions of petroleum are very dissimilar.

As Mr. Topley, F.R.S., took occasion to point out in a recent paper on the Sources of Petroleum and Natural Gas, the American geologists and chemists are agreed that petroleum has resulted from the decomposition of the fossils in the shales and limestones of the Silurian, Devonian, and Lower Carboniferous rocks, chiefly the remains of animals, but in some cases also the remains of plants; that the gas and petroleum thus formed are stored in porous sandstones and limestones, and are prevented from escaping by a covering of impervious shale.

The organic theory may certainly be said to be that which receives the largest measure of support not only in America, and in relation to American petroleum, but in all countries and in relation to all petroleum. It may, however, be safely asserted that the process by which petroleum has been formed has not been the same in all cases. It is quite possible that petroleum may in some cases be of inorganic origin, and the distinguished authorship and support of certain of the inorganic theories is an important feature of the case.

In some instances the petroleum is apparently indigenous to the rocks in which it is found, while in others it appears to be a distillate from strata lying far below the formation in which it is stored.

The not unusual association of mud-volcanoes with petroleum deposits surely cannot be accepted as a proof of the volcanic origin of petroleum, and the outflow of petroleum accompanied by natural gas which occurs in such localities may be due to the action of the volcanic heat upon hydrocarbons formed long ago.

Mr. Ross expresses a doubt whether room could have been found in beds of porous sandstone for the immense

quantities of petroleum raised in America, and he suggests that the oil may have been stored in vast receptacles carved by volcanic water out of former beds of rock salt adjoining the limestone. Dr. T. S. Hunt estimated the amount of oil held in the Niagara limestone of Chicago, and found it to be 4·25 per cent. On this basis the quantity of oil in each square mile of the oil-bearing rock would be 7,750,000 barrels. Again, Mr. J. F. Carll has shown that the pebble sand will absorb 1·15th to 1·10th of its bulk of oil, and this, at a very moderate estimate of the average thickness of the oil-sands in the neighbourhood of Oil Creek, would give a storage capacity of 9,600,000 barrels per square mile, which, as Mr. Peckham has pointed out, is quite adequate to the requirements of the most exceptional cases known. No doubt in some instances the sudden dropping of the tools in the process of drilling indicates the existence of cavities or fissures, but there can be very little doubt that the oil is usually stored in porous rocks.

Mr. Ross states that practical men in this country distrust the permanence of the supply, and hesitate to adopt petroleum for many useful purposes, the object of his paper being to dissipate that distrust by suggesting an explanation of the mystery surrounding the origin of the material. The object is doubtless a laudable one, though in view of the immense undeveloped sources of petroleum, in the existence of which there is good reason to believe, it may be questioned whether the distrust, if it exists, has any good foundation. Obviously it would be satisfactory to feel that the process of formation of petroleum from inorganic substances is now in operation; but the theory which Mr. Ross has propounded is scarcely likely to carry conviction to the minds of any who experience the distrust to which he alludes.

THE REDUCTION OF OXYGEN COMPOUNDS BY MAGNESIUM.
FORMATION OF METALLIC HYDRIDES.
By CLEMENS WINKLER.

THE author recently drew attention to the remarkable behaviour of cerium, which in the nascent state combines very eagerly with hydrogen. Not less striking is the fact that other quadrivalent elements, such as zirconium and thorium, behave similarly, and that also lanthanum, which belongs to the third group, combines with hydrogen as readily as cerium and with exactly the same phenomena.

In accordance with the trivalence of lanthanum, and taking its atomic weight La = 138, the author ascribed to lanthanum hydride the formula La_2H_3, but after vain attempts to combine other members of the third group, such as aluminium and yttrium, and some of the second group, e.g., Ca and Ba, with hydrogen in the same manner, he felt inclined to infer from its surprising similarity of behaviour with cerium that lanthanum might possibly belong to the quadrivalent elements, in which case the formula of lanthanum hydride would be LaH_2.

Meantime, Brauner maintained the trivalence of lanthanum, and the atomic weight La = 138, and his expositions, joined to the author's own researches, induced the latter again to regard lanthanum as trivalent and its hydride as La_2H_3. It appeared that the property of combining in the nascent state with hydrogen belongs not only to lanthanum but to other members of the third group, certainly to yttrium and probably to scandium and ytterbium.

At Brauner's inducement I returned to the members of the second group and again endeavoured to produce their hydrides. Brauner has informed me in a letter under date April 30th last, that he considered the existence of a barium hydride and perhaps of a cæsium hydride as not improbable, pointing out that the discovery of these compounds would form a brilliant confirmation of the periodic law, as there would result the following series—

		I.	II.	III.	IV.
Metal	.. ..	Cs	Ba	La	Ce
Oxide	.. ..	Cs_2O	Ba_2O_2	La_2O_3	Ce_2O_4
Hydride	.. ..	Cs_2H	Ba_2H_2	La_2H_3	Ce_2H_4

or—

$$Cs_4H_2 \quad Ba_4H_4 \quad La_4H_6 \quad Ce_4H_8,$$
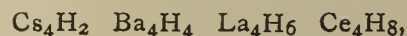
as these hydrogen compounds unquestionably represent polymers of the simple formulæ.

Group I.

As for cæsium and the other members of the first group which here come in question I found it at first impracticable to combine them with hydrogen in the nascent state, i.e., by reduction of their oxides in an atmosphere of hydrogen by means of magnesium. The reduction of the lithium and sodium hydroxides and carbonates takes place with dangerous violence, and that of the corresponding compounds of potassium and rubidium with so considerable a liberation of heat that the hydrides of these metals cannot resist its decomposing action.

Cæsium.—The formation of cæsium oxide, Cs_2O, would be possible only by means of metallic cæsium. As this substance was not at my disposal I confined myself to ascertaining the behaviour of magnesium with cæsium hydroxide and carbonate in an atmosphere of hydrogen.

On heating together a mixture of 150 parts (1 mol.) cæsium hydroxide and 24 parts (1 atom) of magnesium in a current of hydrogen fire appeared, and there was formed behind the boat a metallic mirror consisting chiefly of potassium. The residual sintered mass seemed composed of a mixture of cæsium and magnesium oxides. On operating upon cæsium carbonate the result was similar.

Group II.

It appeared especially important to ascertain the behaviour of nascent metals of the second group with hydrogen, since we had hitherto not the slightest evidence concerning their power of forming hydrogen compounds. Though former experiments had not shown a behaviour similar to that of cerium and lanthanum, I have now the satisfaction of communicating that I have succeeded in combining all the bivalent elements which come here under consideration with hydrogen, at least to a certain degree. This combination ensues in general so slowly that it may at first escape recognition. The heavy metals of the second group, zinc, cadmium and mercury, the oxides of which are reduced by magnesium with explosive violence, could not come into account, the investigation being limited to the metals of the alkaline earths.

The process adopted was in all cases the same. If one of the oxides, e.g., calcium oxide, is heated to redness in an atmosphere of hydrogen, along with the quantity of magnesium powder required for its reduction as it was done with cerium, not the slightest absorption of gas is perceived at first, so that the pinch-cock at the end of the combustion tube must be frequently eased to prevent the liquid in the washing and drying flasks from being forced back. But after the heat has been applied for some time this movement ceases and a few bubbles escape through the washing-flasks. The process varies greatly in rapidity and in some cases has to be continued for hours.

Glucinum and magnesium combined with hydrogen only to the respective extents of 14·96 and of 6·42 per cent. Of calcium 61·52 per cent of the substance operated upon was converted into hydride, and of strontium 94·91 per cent. Barium oxide was converted into hydride to the extent of 94·66 per cent.

From the above facts it appears that all the bivalent elements, in as far as they belong to the class of so-called light metals, are capable of forming hydrogen compounds. The formation is in most cases slow, unattended with striking phenomena, and is effected at moderately high temperatures not exceeding bright redness. Indications are present that a further increase of temperature promotes the formation of hydrides, and besides the disposi-

tion of the elements in question to form hydrides increases directly as their atomic weights.

It seems striking that all the hydrides above mentioned appear as dull, earthy masses, whilst the hydrogen compounds of the alkali metals described by Troost and Hautefeuille, Na_4H_2 and K_4H_2, are silvery white and of a metallic lustre.

It must for the present remain undecided whether the hydrogen compounds of the bivalent elements should have the general formula $R''H$, or R''_2H_2, or R''_4H_4, or if they require a still further multiplication. In any case the proof that such compounds exist is of general chemical interest as well as important as regards the periodic law and the doctrine of valences. But it has a still further significance, since it leads our thoughts and contemplations to the process of creation, to the cosmic structures of different stages of age and development, existing at infinitely higher temperatures than our earth, far advanced as it is in the process of refrigeration. The spectroscope tells us of the very prominent part which hydrogen has played and still plays in the construction of worlds. It reveals to us in the probably hottest stars the presence of just those elements about which we now know that they are able to form hydrogen compounds at very high temperatures,—compounds which are stable in fire.

The same compounds meet us in the sun's atmosphere, which is so much more accessible to spectroscopic examination. If we see in the protuberances escapes of gas, which contain hydrogen, magnesium, and calcium (the last in predominating quantity), the assumption no longer seems unjustifiable that they consist of calcium and magnesium hydrides, even if in a state of dissociation. When projected up to relatively cold elevations they suddenly undergo catagenesis, whereby the marvellously rapid disappearance of these gaseous masses and possibly other phenomena of the sun's surface may be explained. In any case it is an advantage that we can now deal with definite hydrogen compounds of those metallic elements, such as calcium and magnesium, which predominate in the atmosphere of the sun and the other fixed stars.

As Janssen's spectroscopic observations undertaken on the summit of Mont Blanc have shown, oxygen seems absent in the sun or in its gaseous envelope. But even if present it would not exclude the possibility of the simultaneous presence of the above mentioned hydrides of the earthy metals, since these may be permanent and stable at temperatures above the dissociation heat of water. But if we conceive of a heavenly body in a state of heating in which, *e.g.*, calcium hydride can exist along with free oxygen—a heat at which our earth once existed—and if we suppose this orb undergoing refrigeration, a point will be reached at which the calcium hydride ignites with an outburst of flame, exhibiting the spectacle of a burning world, like that seen in 1866 in a star of *Corona borealis*.

And if we consider a more advanced refrigeration such as our earth has already undergone in ages long since past, the combustion product of hydrogen, the water, will begin to react chemically upon the combustion product of the calcium, lime and calcium hydroxide will be formed, or the origin of other calcium salts will be effected with the co-operation of other elements such as carbon or silicon, and the water will remain in excess in a free state, as it has been the case on our earth. Such processes as the last mentioned lie so near our comprehension that we can interpret them, since we can produce them artificially. By the discovery of the heat-resisting hydrides of the earthy metals we may, perhaps, in the future approach nearer to an understanding of the processes in the glowing atmospheres of the fixed stars; and even if this still leaves much scope to the imagination, we must remember that the imagination begins to be permissible in science as long as it is based upon actual observation.—*Berichte der Deutsch. Chem. Gesell.*, vol. xxiv., p. 1966.

A CONTRIBUTION TO THE QUANTITATIVE DETERMINATION OF SULPHUR.

By F. P. TREADWELL.

IN sulphides which are soluble in dilute acids the sulphur is now generally determined either by the oxidation of the liberated hydrogen sulphide, by means of an alkaline solution of hydrogen peroxide, precipitating the sulphuric acid formed as barium sulphate, or the hydrogen sulphide is determined volumetrically, according to Dufusquier and Bunsen iodometrically, or by the alkalimetric process of Eliasberg. These elegant methods, however, are restricted to soluble sulphur compounds. In insoluble sulphides sulphur could not hitherto be determined by the above processes.

The author has found a very simple method, according to which sulphur can be readily expelled from all insoluble sulphides in the state of sulphuretted hydrogen, and determined by one of the above processes. The sulphide, mixed with an excess of iron, is heated for five to ten minutes to dull redness in a current of dry carbonic acid, and the ferrous sulphide formed is decomposed, when cold, by means of hydrochloric acid. A tube of very infusible glass serves for the introduction of the carbonic acid. The iron used is the ordinary commercial "ferrum reductum," which before use is ignited in a current of dry hydrogen. Prior to the determination of the sulphur a blank experiment is made with the materials which are to be used. in order to ascertain their proportion of sulphur. This is done as follows :—

Into a porcelain crucible (made at the Bayeux Works at the price of 30 frs. per hundred) are put 3 grms. of iron powder. The crucible, according to Loewe's proposal, is supported upon a piece of sheet asbestos, in the middle of which there is cut a hole exactly fitting the crucible, which is heated for ten minutes at incipient dark redness in a current of carbonic acid. After being allowed to cool, still in a current of carbonic acid, the crucible with its contents is placed in an Erlenmeyer flask holding about 400 c.c., and provided with a caoutchouc stopper with a double perforation. Through the one aperture passes the gas delivery tube having a small condensation bulb, above which it is bent downwards at an angle of 15°, so that its lower end reaches lower than the bottom of the flask. Through the other perforation passes a tube reaching down to the bottom of the flask and ending above in a globe funnel with a glass cock. The lower end of the gas delivery tube is connected with a Kipp hydrogen apparatus, and a powerful current of hydrogen is passed through for five minutes, whilst the cock of the globe funnel is left open. The cock funnel is then closed, the flexible tube is removed from the gas delivery tube, and the latter is connected with two Fresenius-Vollhard absorption apparatus. The first of these vessels is filled with 50 c.c. of the purest 2 per cent hydrogen peroxide and 10 c.c. of binormal ammonia, whilst the second vessel contains 10 c.c. of ammonia of the same strength. Into the globe funnel are poured 100 c.c. of dilute hydrochloric acid previously boiled (1 : 5), which is slowly let down into the flask. A liberation of gas begins at once and is assisted by a gentle heat, so that three or four bubbles per second pass through the absorbent vessels. In $1\frac{1}{2}$ to 2 hours the development of gas is completed, when a current of pure hydrogen is allowed to pass for half an hour through the globe funnel tube. The contents of the absorbent apparatus are poured into a beaker, covered with a watch-glass, and boiled for fifteen minutes, acidulated with hydrochloric acid, and evaporated to dryness in a porcelain capsule on the water-bath. A few drops of concentrated hydrochloric acid are added to the dry mass, which is dissolved in hot water, filtered, and precipitated with barium chloride.

In the author's experiments the amount of barium sulphate thus found was merely 5 m.grms., which was deducted in the subsequent determinations. In executing

the actual analysis a little iron-powder is first placed in the decomposition crucible, then the substance, then again iron-powder, and the whole is mixed with a platinum spatula. The mixture is covered over with iron-powder, and the operation is completed as in the blank experiment.

The method is applicable to arsenio-sulphates. It cannot be used in the technical analysis of pyrites, as the sulphur present in every combination—*e. g.*, barium sulphate—is determined. In case of arseniferous minerals, &c., hydrogen arsenide is evolved in abundance, whence in such case the escaping gas, after removal of the absorption vessels, is passed into an ammoniacal solution of silver.—*Berichte Deutsch. Chem. Gesellschaft*, vol. xxiv., p. 1937.

DECOMPOSITION OF CHROME ORE BY MEANS OF THE ELECTRIC CURRENT.

By E. F. SMITH.

Two years ago the author mentioned that an intimate mixture of chrome iron ore and melted potassa is decomposed by the introduction of the electric current, and that the chromium oxide present is converted into soluble potassium chromate. The earliest attempts were made with a current of 1 ampère. The oxidation of the mineral was apparently completed in 15 minutes, but the wish to economise time by increasing the current led the author astray, and many decompositions, fruitless as well as successful, were made before the most satisfactory conditions were ascertained. It was found that a more powerful current acted chiefly upon the oxides of iron contained in the ore and the potassa employed, liberating larger or smaller portions of the respective metals. The occurrence just mentioned seems to take place after a partial decomposition of the mineral, so that a little of the chrome ore always remains undecomposed.

The following method was found after many experiments to give good results:—

Method of Oxidation.—30 to 40 grms. caustic potassa are brought to fusion in a nickel crucible 1⅞ inches in height and 2 inches in width, and gently heated until the excess of water is evaporated. The crucible is then set upon a heavy ring of copper wire in connection with the anode of a battery.

During the decomposition the crucible is gently and uninterruptedly heated by means of a small flame. The mineral is weighed out upon a watch-glass and is then carefully placed upon the liquid potassa by means of a camel's hair pencil. The crucible is covered with a perforated watch-glass, and the platinum rod connected with the cathode of the battery is let down into the melted mass, thus producing the current. Portions of the melted mass are projected against the under side of the watch-glass, but the liquid soon collects in drops and falls back into the crucible, and thus restores any traces of ore which have been projected upwards by the bursting of the gas bubbles.

Experience shows that it is preferable to use the crucible itself as an anode. Before the current is finally interrupted it must be reversed by means of a commutator, which is left permanently in the current along with a Kohlrausch ampère-meter. This is necessary because metal is deposited upon the cathode and contains particles of ore which are thus withdrawn from the oxidising process. By reversing the current these particles of ore are set at liberty and made capable of oxidation.

The quantity of ore to be taken for analysis varies from 0·1—0·5 grm. The ore used for oxidation must be ground quite fine. In the author's experiments the ore was never used in such a fine state of comminution as is prescribed in order to obtain a complete decomposition by other methods.

For the quantity above indicated the current must not exceed 1 ampère. As for the time needed for oxidation the quarter of the ore is indubitably decomposed in 15 minutes, but to effect a complete decomposition of the ore a time of 30—40 minutes is recommended. Much depends on the resisting power of the sample. In this respect chrome ores vary exceedingly,—a difficulty which has to be overcome in every method for their analysis. Half an hour at least should be allowed for completing an oxidation by this method.

As the decomposition proceeds the melted potassa takes a deeper yellow; the part which climbs up on the edge of the crucible and the watch-glass resembles a cauliflower.

The current may now be interrupted. When this has taken place the platinum rod (the cathode) is lifted out the liquid, the watch-glass is carefully lifted off the crucible with nickel forceps, its lower surface is rinsed with water, and the washings are collected in a beaker. The crucible is then removed from the copper ring and set upon a marble plate to cool. The platinum cathode must also be washed with water. It appears black in consequence of the deposit of metallic iron which has been formed upon it.

It is judicious to dissolve this coating in dilute hydrochloric acid in order to be satisfied that no undecomposed ore is present in it.

When the crucible is cold it is placed in a beaker holding about 300 c.c., covered with water, and set to digest upon a warm plate. In a few minutes the contents of the crucible are entirely dissolved and the crucible itself may then be removed from the liquid. It contains, beside an excess of potassa, potassium aluminates, silicates, manganates, and chromates. The insoluble matter in suspension consists chiefly of iron oxide.

After the alkaline solution has been heated for a time on the plate, the insoluble part is filtered off and *thoroughly* washed in boiling water. The vessel containing the soluble salts is set aside, and the portion insoluble in water is treated with hot hydrochloric acid. It must dissolve completely without leaving a residue. If this is not the case the decomposition is incomplete.

Determination of the Chrome.—The chrome in the yellow alkaline filtrate may be determined either gravimetrically or volumetrically. In his more recent determinations the author used exclusively the latter method. For this purpose the chromic solution was acidified with sulphuric acid, and a weighed quantity of ammonium ferrous oxalate was added. An excess of the latter was determined by normal potassium bichromate. Potassium ferrocyanide was used as reagent. In some cases the excess of ferrous salts was determined with a solution of potassium permanganate, but this method was abandoned, as the final reaction could not be recognised with sufficient exactness. — *Berichte der Deutschen Chem. Gesellschaft*, vol. xxiv., p. 2182.

PROPERTIES OF PRECIPITATES, &c.*

By E. WALLER, Ph.D.

K_2PtCl_6.

Rem.—Precipitant, $PtCl_4$.

More strongly coloured than the corresponding ammonium salt, but otherwise resembling it in general characters. Like that compound, it is sometimes dissolved in hot water, and the solution evaporated in a weighed capsule so as to dispense with weighed filters.

Cond.—Solution should be cold, alcoholic, and should contain preferably only sodium salts other than KCl.

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* From *School of Mines Quarterly*, xii., No. 3.

Chlorides or HCl should be present. Small amounts of Mg or Ca are permissible, though disadvantageous.

Sol.—Somewhat soluble in cold, more so in hot water. Insoluble in strong alcohol and in ammonium salts. Solubility increased by acid or alkali, diminished by $PtCl_4$ or Na_2PtCl_6.

Contam.—NaCl and other salts (as sulphates) not soluble in alcohol. Such contaminants are most readily removed by washing with aqueous solution of NH_4Cl, previously saturated with K_2PtCl_6.

Ign.—Alone, it is imperfectly converted to KCl and spongy platinum; with a reducing agent (as $H_2C_2O_42H_2O$), the conversion is complete. The heat should not be too rapidly raised. If ignited in platinum, too high a heat may fuse the finely-divided metal to the platinum vessel. After ignition, the KCl formed must be washed off with water before weighing.

NaCl.

Rem.—See *Rem.* under KCl.

Cond.—As for KCl.

Sol.—Soluble in water; much less so in strong HCl or alcohol. Less soluble in these menstrua than KCl.

Contam.—KCl (see KCl) or other non-volatile salts.

Ign.—Decrepitates violently on heating unless very thoroughly dried. Fusible at full red heat, and volatilised at a temperature but little above its point of fusion. The temperatures of fusion and volatilisation are, however, perceptibly higher than with KCl. Becomes slightly alkaline on fusion from loss of Cl.

Na_2SO_4.

Rem.—The suggestions as to K_2SO_4 throughout are applicable also to Na_2SO_4 (see K_2SO_4), even to the formation of $NaHSO_4$ by evaporation with excess of H_2SO_4 and ignition.

CaC_2O_4.

Rem.—Usual precipitant $(NH_4)_2C_2O_4$. The solution of the reagent had best be boiling hot when added. Precipitated cold or in very dilute solutions, it separates in a very fine powder. In any case, boiling for a short time and then adding a few drops of ammonia is advisable before proceeding to filter. If precipitated in boiling alkaline solution, the solution bumps vigorously. Enough oxalate should be added to convert all Mg present into $Mg_2C_2O_4$.

Cond.—Best precipitated in a boiling neutral solution, which should contain only Mg and alkalies besides the Ca.

Sol.—Dissolved by mineral acids, slightly soluble in acetic. Somewhat soluble in $MgCl_2$. Insoluble in MgC_2O_4. From its solutions in mineral acids, ammonia or other alkalies precipitate it unchanged.

Contam.—MgC_2O_4, which is removed by re-solution in HCl and re-precipitation by ammonia. If the proportion of Mg present is large, this re-solution and re-precipitation may have to be repeated two or three times. Precipitation in a solution *barely acid* with HCl is most effective in separating from Mg.

Ign.—Affords first $CaCO_3$, afterward CaO. Under ordinary circumstances the product is a mixture of the two. To obtain CaO it is necessary to ignite for some time over a blast lamp. To obtain $CaCO_3$, it is ignited moderately, and repeatedly moistened with ammonium carbonate, and gently ignited after each addition.

Ignited with H_2SO_4 it affords $CaSO_4$, which is frequently partially reduced to CaS by ignition with C, requiring further treatment with H_2SO_4 and ignition. The easiest mode of management is to transfer the filter paper containing the precipitate still wet to an ordinary fusion crucible, and wet down with concentrated nitric and sulphuric acids. Then expel the excess of acid with a gentle heat, and finally ignite. A second treatment with H_2SO_4 is often necessary. Instead of H_2SO_4, a strong solution of $(NH_4)_2SO_4$ containing free ammonia and about 2 grms.

NH_2Cl per 100 c.c. has been recommended (*vide* Crookes's "Select Methods," Second Edition, p. 47).

$CaCO_3$.

Rem.—Usual precipitant $(NH_4)_2CO_3$. For separation or determination of CO_2, the reagent is $CaCl_2$ with ammonia. Usually obtained for separation. At first it separates in flocculent or amorphous form, but after a short time assumes a crystalline form. This change is hastened by warming gently.

Cond.—Large proportions of alkaline salts, especially citrates, and of magnesium salts, should be avoided. An alkaline solution is of course necessary.

Sol.—Soluble in water containing CO_2; very soluble in all acids; decomposed and dissolved by NH_4Cl, slowly in the cold, quickly if hot. Insoluble in water containing ammonium carbonate with ammonia.

Ign.—Converted to CaO as described under $Ca_2C_2O_4$. The change is more readily effected if some carbon is mixed with it.

$MgNH_4PO_4$.

Rem.—Usual precipitant for Mg, Na_2HPO_4; for P_2O_5 (ortho), "magnesia mixture," preferably that made with $MgCl_2$.

Should be crystalline; if flocculent, some contaminant is present. When the proportion of precipitate which can form is small relatively to the bulk of the solution, some hours are necessary for complete separation.

Completeness of precipitation much accelerated by cold and agitation.

When washed as usual with diluted ammonia, alkaline phosphate (Na_2HPO_4, &c.) is not very rapidly removed, the salt being less soluble in ammonia than in water.

Cond.—Absence of silica or any bases other than alkalies. NH_4Cl or ammonium salts should be present.

Sol.—Solution should be cold for precipitation and filtration. Soluble in acids, even when weak, in hot solutions, and to some extent in cold water; insoluble in dilute ammonia.

Contam.—Silica and $Mg(OH)_2$ or basic salts of Mg. The latter is only likely to occur when the precipitate is used for the purpose of determining P_2O_5 or P. The difficulty is avoided by adding the Mg mixture (preferably the chloride) slowly with stirring. Silica may be weighed and deducted after ignition, weighing and dissolving in acid. MoO_3 may also occur when the molybdate separation has preceded.

Ign.—Should be well dried before igniting. If heated too rapidly some loss may result from too rapid decomposition. If the filter paper is allowed to burn with flame, some particles of the precipitate (in weighable amount) may be mechanically carried off. The precipitate has afterward a tendency to sinter together at a moderately high heat, thereby preventing the oxygen of the air from penetrating the mass and oxidising the carbon, the precipitate being left grey or black. The best mode of managing is to expose the precipitate for some time to a dull red after the carbonisation of the paper, and finally finish with the full heat of the Bunsen burner. If the precipitate comes black repeated moistening with nitric acid and cautious ignition is to be recommended.

$Mg(OH)_2$.

Rem.—Usual precipitant $Ba(OH)_2$ for separation from alkalies when these are to be determined. The $Ba(OH)_2$ should be tested for NaOH, which is not infrequently present.

Cond.—Alkaline solution moderately concentrated, containing no NH_4 salts.

Sol.—Dissolved by acids or ammonia salts. Precipitation partly prevented by presence of organic salts, citrates, tartrates, sugar, &c.

Contam.—Usually unimportant, the object generally being to remove from the solution MgO and all substances except those readily separable by ammonium carbonate.

$BaSO_4$.

Rem.—Precipitant for SO_3, $BaCl_2$; for Ba, H_2SO_4.

Precipitated in an extremely fine state of division (runs through filter paper) if formed in cold or dilute solutions, or such as contain ammonia salts. Forms slowly if small in amount.

The tendency of the precipitate to creep up the side of a beaker may be checked by adding a drop of HCl.

Cond.—Hot solution acidified with HCl. Hydro-fluo-silicic acid or silica should be absent, also large proportions of calcium salts, or salts of the $(NH_4)_2S$ group of bases.

Sol.—Soluble in concentrated H_2SO_4, in HCl when moderately strong and hot, and in HNO_3 even when tolerably dilute. It is also soluble in hot Fe_2Cl_6, in alkaline and alkaline earth nitrates, citrates, and salts of some other organic acids.

Insoluble in water, in very dilute HCl, and in acetic acid.

Contam.—The especial difficulty with $BaSO_4$ is its tendency to carry with it other substances, as alkaline and alkaline earth nitrates, chlorates, sulphates, and chlorides. Potassium salts give more trouble in this respect than sodium salts. The precipitate may also contain silica, and basic ferric, aluminic, or chromic compounds.

Repeated boiling up with very dilute HCl assists in removing some of these to a considerable extent, though there is some danger of dissolving some of the precipitate by this treatment. Washing alternately with hot dilute HCl and with cold water is often advantageous. Stolba's method of purifying the precipitate consists in digesting (after washing) for ten to fifteen minutes at a boiling heat, with 40—50 c.c. of cold saturated solution of $Cu(C_2H_3O_2)_2$ and acetic acid, filtering, and washing free from Cu (*vide* Crookes's " Select Methods," second edition, p. 492). Sloane recommends for purification from iron, to decant the supernatant liquid closely, then add 5 or 10 c.c. of concentrated HCl, and boil for one minute, dilute, and after nearly neutralising with ammonia, filter and wash thoroughly (*Jour. Amer. Chem. Soc.*, iii., 37). Archbutt advises to precipitate warm (not boiling), allow to stand until thoroughly cold and the precipitate has settled well, then to filter and wash with cold water (*Jour. Soc. Chem. Ind.*, ix., 25). Jannasch and Richards assert than no correct determination of SO_3 can be made in the presence of Fe, because the precipitate always contains more or less of a double barium iron sulphate, from which SO_3 is expelled on ignition. To avoid errors they therefore recommend the previous removal of the iron by ammonia (*Journ. Prac. Chem.*, [2], xxxix., 321), (*vide* also Lunge, *Zeit. Angew. Chemie*, 1880, 473). Zeigler (*Pharm. Central.*, 1881, p. 555) recommends the addition of some $AgNO_3$ to the solution (containing chloride), that the AgCl may enclose and carry with it the particles of $BaSO_4$. After washing with water the AgCl may be dissolved off with ammonia.

Ign.—With C some BaS invariably forms. The difficulty may be remedied by adding a few drops of fuming HNO_3 to re-oxidise the S, and igniting again, or better by re-igniting after the addition of a drop or two of concentrated H_2SO_4.

$BaCO_3$.

Rem.—At first amorphous, it assumes almost immediately the crystalline form, in which condition it does not affect alkalimetric indicators.

Cond.—Alkaline solution.

Sol.—Soluble in water containing CO_2 and in acids. Also taken into solution by NH_4Cl and some other ammonium salts, especially on boiling. Insoluble in a mixture of ammonium hydrate and carbonate.

Contam.—$MgCO_3$ if much is present, and carbonates of fixed alkalies if present.

Ign.—Converted imperfectly to BaO, unless mixed with carbon, when the change occurs readily.

(To be continued.)

SIMPLEX GAS GENERATOR.

By C. G. MOOR.

THIS new pattern gas generator possesses several advantages over those now in use. It may be used equally well to prepare hydrogen, carbonic acid gas, chlorine (using the compressed chloride of lime), or sulphuretted hydrogen.

The last-mentioned can best be prepared by using commercial hydrochloric acid mixed with an equal bulk of water. The apparatus is easy to clean and charge, delivers a drier gas than most other forms of generator, and the liquid cannot travel up the gas tube. The parts may be had separate.
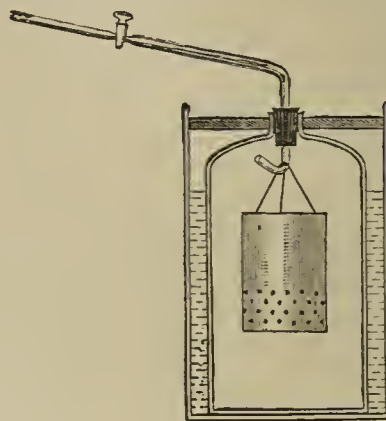
To charge, take out bell-jar and unhook perforated pot, fill it with the solid and replace, pour acid into outer jar till about half full.

The solid may be any size or shape provided it is not dust. Any part of the apparatus can be had separately to replace breakages.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING SEPTEMBER 30TH, 1891.

By WILLIAM CROOKES, F.R.S.;

WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford;

and C. MEYMOTT TIDY, M.B., F.C.S., Barrister-at-Law,
Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, Metropolis Water Act, 1871.

London, October 8th, 1891.

SIR,—We submit herewith the results of our analyses of the 181 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from September 1st to September 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 181 samples examined, the whole were found to be clear, bright, and efficiently filtered, excepting one, which was recorded as " very slightly turbid."

The satisfactory condition of the water supply to the Metropolis, recorded now for several consecutive months,

continued to be maintained during the month of September; although, indeed, the individual results obtained exhibited a somewhat greater degree of variation than has been noticeable for some time previously. Thus in the case of the Thames-derived supply, the mean proportion of organic carbon was found to be 0·129 part in 100,000 parts of the water, with a maximum of 0·150 part in any single sample examined; while the mean amount of oxygen absorbed was found to be 0·076 grain per gallon of water, with a maximum of 0·145 grain in any single sample examined. The highest results were afforded by the examinations made during the middle of the month; and the figures resulting from the separate modes of examination were less closely parallel than usual, those expressing the amounts of oxygen absorbed agreeing best with the determinations of the colour-tint of the water.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
WILLIAM ODLING.
C. MEYMOTT TIDY.

ON THE OCCURRENCE OF NITROGEN IN URANINITE, AND ON THE COMPOSITION OF URANINITE IN GENERAL.*

By W. F. HILLEBRAND.

General Introductory Remarks.

WHEN the work which is described in the following pages was commenced in 1888 it was simply as an analysis of a fragment of a large crystal of uraninite from Glastonbury, Connecticut, without thought of further extension. Thoria had been found in it, and quantitative analysis was made in order to learn if possible whether this belonged to the uraninite or was due to an accidental admixture of thorium silicate as found by Penfield (*Am. Jour. Sci.*, [3], 1882, xxiv., 250) to be the case, at least in part, for the thoria in monazite from Portland, Connecticut, and Amelia County, Virginia. It was hereby established that the 10 per cent of thoria found was a constituent of the uraninite, and the unexpected discovery was made that no formula in the slightest degree corresponding to that found by Comstock (*Am. Jour. Sci*, [3], 1880, xix., 220) for the Branchville, Connecticut, uraninite, and by Blomstrand ("Geol. För. Förh.," 1884, vii., 59, and *Jour. Prakt. Chem.*, 1884, xxix., 191) for the Norwegian and Bohemian varieties, could be assigned to this from Glastonbury. The hitherto unanalysed uraninite formerly found at Black Hawk, Colorado, was then examined, and was likewise not referable to the orthouranate formula of Blomstrand. No thoria was found in it, but instead about 7 per cent of zirconia. In both cases about 60 per cent of UO_2 had been found, whereas the highest percentage given by any other analyst was in the neighbourhood of 54 per cent for the Branchville variety. My own experiments had shown such extraordinary variations in the percentages of UO_2 found by the ordinary method of decomposing with sulphuric acid in sealed tubes filled with carbonic acid, and titrating with potassium permanganate, that a re-examination of the Branchville mineral seemed desirable. Profs. Brush and Dana, of New Haven, very kindly placed at my disposal the remainder of their material from that locality, it being the same lot from which Comstock had selected his sample for analysis. While different samples showed different amounts of UO_2, the results were from 10 to 18 per cent higher than Comstock's, and, moreover, about 7 per cent of thoria was found which had been entirely overlooked by him. This latter, as in the Glastonbury mineral, was not referable to any thorium

silicate, nor to a phosphate, but belonged to the uraninite. Comstock's formula, $3RO_2+2RO_3$, for the Branchville uraninite was of course hereby invalidated. Of North American occurrences of this mineral it only remained to examine that from North Carolina. From the Black Hills, Dakota, where it has been reported to occur, I have been unable to procure specimens, and the same can be said of the—at that time unknown—Llano County, Texas, locality, whence a closely allied mineral, nivenite, has recently been described by Hidden and Mackintosh (*Am. Jour. Sci.*, 1889, [3], xxxviii., 482). Owing to its evident alteration it was not expected that light would be thrown on the question of original composition by an examination of the North Carolina material, but the presence or absence of thoria could be ascertained, as it was affirmatively by finding that and other earths.

In view of what had thus been learned regarding the uraninites of this country it seemed advisable to re-examine the European varieties. Specimens from Przibram, Joachimsthal, and Johanngeorgenstadt contained no rare earths whatever, but they were so contaminated with carbonates and sulphides, and some combination of vanadium, that it seemed for the present useless to attempt an estimation of UO_2 in them. Through Prof. F. W. Clarke, of the U.S. Geological Survey, there were obtained from Prof. A. E. Nordenskiöld specimens marked cleveite from four localities near Moss, Norway, and to Prof. W. C. Brögger are due my thanks for specimens of Blomstrand's original bröggerite, and of the supposed thorium-free uraninite analysed by Lorenzen ("Geol. För. Förh.," vi., 744), and quoted by Blomstrand (*Journ. Prakt. Chem.*, 1884, xxix., 223 ff.) as a striking proof of the correctness of his view that all varieties of unaninite may be referred to the orthouranate type. These six samples contained, without exception, thoria and other earths, in no case less than 8 per cent, and the four from Prof. Nordenskiöld, with one exception, proved not to be cleveite. Notwithstanding certain variations in composition they were evidently one and the same mineral, just as were those from Branchville and Glastonbury; and the Norwegian and Connecticut varieties, though differing greatly in their relative proportions of UO_2 and UO_3 and in their resistance to the solvent action of acids, were manifestly specifically identical.

These analyses had been practically completed, and a portion of the results very briefly communicated to the public from time to time (*Am. Jour. Sci.*, 1888, [3], xxxvi., 295; *Bull. U.S. Geol. Survey*, No. 60, 1887-1888, p. 131), when, in consequence of a certain observation and its results, an entirely new direction was given to the work and its scope wonderfully broadened. This was the discovery of a hitherto unsuspected element in uraninite, existing in a form of combination not before observed in the mineral world. As already published (*Am. Jour. Sci.*, 1889, [3], xxxviii., 329, where, by a typographical error, UO_2 is made to read NO_2) all tests unite in showing that this element is nitrogen, which is given off in a gaseous form on heating the mineral with a non-oxidising acid, or, as ascertained later, by fusing it with an alkaline carbonate.

It is very unfortunate that this discovery of an escape of gas when treated with an acid, or rather the recognition of its important bearing, for the observation was made at an early date, did not occur sooner; for then more satisfactory results could have been obtained with the — in more than one respect—most valuable material from Branchville, and nearly all the analyses would have been carried out with the most painstaking care, in order to secure the utmost possible accuracy in summation, the importance of which will appear in the sequel. Inasmuch as the analyses were made solely with a view to ascertain the percentages of rare earths and the relative proportions of UO_2 and UO_3, where a variation of half a per cent, or even more, from the true summation was of very little consequence, that extreme care in the preparation and use of reagents and in analytical manipulation which

subsequently acquired knowledge showed to be so necessary was not exercised. Partly in consequence of this, and partly because of the length of time required for these investigations, caused by a want of abundant material, which necessitated oftentimes awaiting the result of one experiment or analysis before venturing upon another, it has been impossible to bring this investigation as far forward as was expected. So much time has elapsed since it was begun, and results of so much importance have been achieved, that it seems advisable to make them public now in detailed form, incomplete as they are in some respects and difficult of interpretation in certain directions.

Before proceeding to discuss the analyses themselves it is necessary to give in some detail the methods of analysis pursued, in order that the degree of credence to be accorded the results may be fairly weighed, and to present the evidence upon which the gas obtained from uraninite has been pronounced nitrogen.

Preparation of Samples for Analysis.

As a prelude to the description of analytical processes employed, the manner of freeing the sample as far as possible from adhering gangue may be briefly described. The specimens consisted, except in the case of the amorphous Colorado, Bohemian, and Saxon varieties, of crystals and crystal fragments more or less coated and invaded by a felspar or mica, or both, sometimes by columbite or a little quartz, and the surfaces opened up by fractures were often more or less coated with a reddish infiltration product which was little, if at all, soluble in the weak nitric acid employed for dissolving the uraninite on commencing an analysis. The sample was reduced to two or three grades of fineness by crushing and passing through several small sieves superposed one upon the other, care being taken to form as little fine dust as possible. When all had passed the coarsest sieve the different fractions were washed by decantation to free from dust, and then carefully panned in watch-glasses of suitable sizes. By this means all the mica and the greater part of the other lighter impurities were removed, and a very fair degree of purification was reached. The columbite, if present, remained mostly with the uraninite, but caused little subsequent trouble. When no more gangue could be panned out without too great loss of material the different portions were united, the specific gravity of the combined sample dried at 100° C. was taken, and it was then finely ground. The fine dust formed in the preliminary crushing was not used, unless for qualitative work, being generally too much contaminated with gangue. The panned material was always examined under the lens when dry, and aside from an occasional adhering reddish fragment appeared clean and free from foreign bodies.

(To be continued).

PROCEEDINGS OF SOCIETIES.

SOCIETY OF CHEMICAL INDUSTRY.
(LONDON SECTION).

This Section meets at the Chemical Society's Rooms, Burlington House.

Chairman—T. Tyrer.
Vice-Chairman—W. Crowder.
Committee—C. F. Cross, J. Dewar, A. G. Green, S. Hall, C. W. Heaton, J. Heron, D. Howard, W. Kellner, B. Redwood, W. S. Squire, G. N. Stoker, F. Napier Sutton, Wm. Thorp, T. E. Thorpe.

Communications to be sent to T. Tyrer, Stirling Chemical Works, Abbey Lane, Stratford, E.

Probable Arrangements.

Nov. 2nd, 1891 (Monday):— Mr. W. C. Young, "On Volatile Organic Matter in Potable Water and a Simple Method of Estimating Volatile and Non-Volatile Matter in Water." Dr. S. Rideal, "Some Experiments on Solidifying Petroleum."

Dec. 7th :—Mr. Watson Smith, "A Contribution to our Knowledge of the Soluble and Resinoid Constituents of Bituminous Coals." Dr. Murray Thompson, " The Salt Industry of India."

Jan. 4th, 1892 :—Mr. Boverton Redwood, " The Gallician Petroleum Industry."

NOTICES OF BOOKS.

An Elementary Handbook on Potable Water. By FLOYD DAVIS, M.Sc., Ph.D. New York, Boston, Chicago: Silver, Burdett, and Co. London : Gay and Bird. Small 8vo., pp. 118.

THIS book does not by any means cover the same ground as the well-known treatise of Messrs. Wanklyn and Chapman. There are no instructions for the quantitative analysis of water or for its microscopical or bacteriological examination. The nine chapters treat successively of pure water, inorganic constituents, vegetable constituents, animal constituents, micro-organisms, water supplies, natural purification, artificial purification, and systems for central filtration. An appendix enlarges on the " Origin and Home of Cholera," and gives a few rough tests for the recognition of impure waters, such as the permanganate, the silver nitrate, Heisch's sugar test, and Pasteur's microzyme test.

There is here very little to which exception can be taken. Scarcely sufficient justice seems to be done to the action of green chlorophyllaceous vegetation in purifying water by means of the oxygen which it liberates. Nor can it be safely inferred that sewage fungus (*Beggiatoa alba*) is an indication of organic pollution. It is found flourishing luxuriantly in the water of sulphur springs and in the drainage of certain chemical works. The pollution of English streams is painted in a very exaggerated style. Says the author :—" The waters of many where city sewage enters them are actually offensive, and during the summer months, owing to the stench, the passenger traffic is forced to the railways." Polluted waters are not uncommon in England, but we never have met with a place where passenger traffic is " forced to the railways " as above stated.

The purification of polluted rivers as they flow is something more than apparent, as it is proved both by chemical analysis and by observation of the organisms found in the water. The conclusion of the Royal Commissioners given here in a foot-note (or at least of the one Commissioner entitled to form a conclusion) is only in part justifiable. If the English rivers do not purify themselves, it is not a question of their length, but of the volume of sewage in proportion to the river water, and of the constant supplies of pollution which enter every few miles.

What is here said, and very truly said, concerning the inability of the soil to hold back pathogenic bacteria, agrees ill with the methods proposed for supplying cities with water. Such are the ground-water system, or the filtering gallery. It is not often that a well of 40 feet in depth in or near a city is secured by an impervious stratum against the entrance of sewage. The " national system " depends on the use first of precipitants, then, if needed, of filtration, and lastly, of aëration with compressed air under high pressure.

Cholera is traced to the armies of pilgrims frequently traversing India under the most anti-sanitary conditions.

This is perfectly correct; but it should also have been mentioned that pilgrimages from India to Mecca spread the evil westwards, especially as the devotees encounter at the shrine of the prophet other pilgrims from Egypt and the northern coast of Africa. These facts show the folly of expecting to arrest the spread of cholera to Europe by any system of quarantine at Suez. These destructive pilgrimages could be arrested only, if at all, at the cost of a war infinitely worse than the Sepoy mutiny.

Burdett's Hospital Annual and Year Book of Philanthropy, 1891—1892. Containing a Review of the Position and Requirements of the Voluntary Charities, and an Exhaustive Record of Hospital Work. Edited by HENRY C. BURDETT. London: The Hospital (Lim.), 140, Strand, W.C.

THERE is in this volume much which, of necessity, withdraws itself from our view as being economical or political rather than scientific. Such subjects are the policy, and, indeed, the very existence, of the Asylum's Board, the management of different hospitals, and the extent to which such charities are abused by persons well able to pay for private medical attendance. We cannot, however, avoid being painfully struck by the facts that not a few of these institutions are unable to pay their way, and that in many cases beds, and even entire wards, remain unoccupied or closed from the lack of funds. Nor is the amount of disease evidently existing a subject to be passed over lightly. It might probably be a good investment of money and energy if we attended less to the cure of disease and more to its prevention, and if we included in the "preventible" class many affections which are certainly not contagious.

We doubt whether the author has acted advisedly in contrasting the respective conditions and efficiency of the hospitals of Oxford and of Derby, and of holding up the former to censure. We should be apt to think that Derbyshire is far wealthier than Oxfordshire. The proposal to exclude from any share in the proceeds of Hospital Sunday those "Surgical Appliance" or "Aid Societies" which require applicants to canvass for tickets is timely and wholesome.

The canvassing system, indeed! Unless we are misinformed, a "pushing" contemporary has opened a department for the purchase, sale, or exchange of admission tickets.

It is well known that medical establishments which are to all intents and purposes private speculations sometimes figure under the guise of hospitals. Hence the work before us is perfectly justified in suggesting that this should be stopped by law.

The author tells us in his chapter on nurses and nursing that "every boy in his teens wants to be a sailor; every girl in her teens wants to be a nurse." Which of the branches of this dictum is the more exaggerated it would be hard to decide.

A remark is made that "massage has no business to be regarded as a branch of nursing, but unluckily it constantly is." If advertisements are to be believed, proficiency in massage is growing to be required from governesses and lady-helps!

Under the rubric institutions and associations we find mentioned not a few of the most pronounced "anti" type, and having certainly little visible connection with hospitals. Thus we find a "Brown Institute," for the study and treatment of domestic animals, with an income of £1000, a home for stray dogs and cats in receipt of £3000 (!), and two Anti-vivisection Societies, the collective incomes of which reach the total of £2300. On the contrary, the "Society for the Promotion of Medicine by Research" is ignored.

We are very glad to find that the electric quacks, now so thriving, do not here figure in the character of philanthropists.

CORRESPONDENCE.

THE CONSTITUTION OF BUTTER, &c.

To the Editor of the Chemical News.

SIR,—In his letter (CHEMICAL NEWS, vol. lxiii., p. 201) Mr. Wanklyn takes exception to my statement that "Messrs. Wanklyn and Fox have never published a single original experiment in support of their assertion that the proportion of glycerin yielded by saponification of butter and other fats exhibits any grave departure from the amount required by the accepted view of their constitution."

Notwithstanding Mr. Wanklyn's denial, the above statement is, I believe, perfectly correct as it stands. If I had stated that "neither Mr. Wanklyn *nor* Mr. Fox had ever published" I should have been in error. Mr. Fox has not published anything of the kind to my recollection, and it is only fair to say that he has taken no share in Mr. Wanklyn's recent resuscitation of the isoglyceride theory. But Mr. Wanklyn did describe, in a paper read by him before the Society of Chemical Industry in January last (*Journal,* x., 89), *a single experiment* which he had made in 1883, but had not previously published.

I am sorry that Mr. Wanklyn did not remind me of this one solitary experiment when I made the statement, to which he he now takes exception, in his presence some months since. It was certainly with no intention of inadequately stating Mr. Wanklyn's case that I omitted to mention the matter in my paper printed on page 179. At the meeting of the Society of Chemical Industry at which Mr. Wanklyn read his paper the experiment was very strongly criticised, as being badly devised and inconclusive in several respects, and Mr. Wanklyn made no sufficient answer to the objections then raised. Mr. Wanklyn's detailed account of the experiment, as printed in the *Journal of the Society of Chemical Industry,* contains abundant internal evidence of the—to put it mildly —inconclusive nature of the experiment, as I am quite prepared to show if required. I am therefore somewhat surprised that Mr. Wanklyn still lays stress on the experiment, and regards it as lending support to his theory. The result is absolutely inconsistent with the more recent experience of various independent observers, and Mr. Wanklyn would have been wise to allow the record of the experiment to remain in his note-book, where he had already let it rest for seven or eight years.

Since the appearance of Mr. Wanklyn's letter I have attempted to repeat his experiment of heating slaked lime with butter-fat, but have met with a practical difficulty in which I shall be glad of his advice. Mr. Wanklyn kept the mixture on the water-bath for a "long period," stirring constantly. My experiment has now continued for nearly forty hours, and my stirring powers are exhausted; in fact, they long since degenerated from "constant" to "frequent," and from that to "occasional." Under these circumstances I started a fresh quantity in a closed flask in the water-oven. This flask has been frequently shaken during several days, but there is no apparent sign of saponification having taken place. It appears still to be simply melted butter, with slaked lime in suspension. How long did Mr. Wanklyn's constant stirring continue? Where am I wrong, and when am I to regard the saponification as complete?

Dr. William Johnstone writes:—"Mr. Allen charges me with having stated that *tallow* required 23 per cent of caustic potash (KHO) for its saponification, against 19·3—19·8 per cent as the united experience of other observers. I never said or wrote anything of the kind; the statement is purely a misrepresentation." This is rather a strong denial, and somewhat more positive than the facts warrant. What I stated (page 182) was that Dr. Johnstone had "*recently published experiments*

(*Analyst*, xvi., 26) according to which tallow requires 23 per cent of caustic potash, &c." For "tallow" read "beef fat," which is practically synonymous, and my statement is absolutely correct; and seeing that the united experience of other observers is that "beef fat," equally with tallow, requires from 19·3 to 19·8 per cent of potash for its saponification, Dr. Johnstone's experience that 23 per cent is required is almost as unaccountable as his correction was unfair and unnecessary. Dr. Johnstone's position is similar to that of a man who has stated that he was born in 1868, and then objects to others holding that his age is now twenty-three.

Dr. Johnstone's reference to Mangold's recent results, and his claim that they furnish "an unexpected confirmation" of his own statements, have already been dealt with by Mr. Hehner. Whether or not butyric acid is oxidised to oxalic acid under exceptional conditions is beside the question. Mangold's results, like my own experiments, absolutely contradict Dr. Johnstone's statement that Benedikt and Zsigmondy's process for determining glycerin by oxidation to oxalic acid by alkaline permanganate is rendered inaccurate by the presence of butyric acid. Neither does Mangold in any way endorse the "eccentric equation" $C_4H_8O_2 + O_6 = 2C_2H_2O_4 + H_4$, according to which Dr. Johnstone appears to hold that free hydrogen is evolved in presence of excess of alkaline permanganate.

The other remarks of Dr. Johnstone scarcely call for comment. As the estimation of glycerin by bichromate, which I quoted as having yielded 11·83 per cent on the butter, was made on an acidulated liquid which had already been distilled to a small bulk, the "volatile fatty acid which readily reduces acid bichromate" could scarcely have interfered. No one contends that the oxidation processes of estimating glycerin are reliable in all cases—in fact, I have stated exactly the opposite.

Similarly, no one doubts that, under very extreme conditions chromic acid, and possibly alkaline permanganate, will oxidise butyric to carbonic acid; but that is not the point at issue.—I am, &c.,

ALFRED H. ALLEN.

Sheffield, October 24, 1891.

BEHAVIOUR OF BUTYRIC ACID WITH ALKALINE PERMANGANATE.

To the Editor of the Chemical News.

SIR,—In reply to your correspondent, Mr. Otto Hehner (CHEMICAL NEWS, vol. lxiv., p. 212), I decline the compliment and the reproach as well as his literal translation, and beg to inform him that I quoted from an English translation of Mr. Mangold's paper, made by a German whose knowledge of the English language is infinitely superior to that of your correspondent's, and is as follows:— Mangold, speaking of his modification of Benedikt and Zsigmondy's method, says "The presence of butyric acid does not affect the result, since butyric acid does not become oxidised in the *cold* by an alkaline solution of permanganate; *butyric acid yields oxalic only when boiled for a considerable time with an excess of alkali and potassium permanganate.*"

Mangold's experiments are made upon pure glycerin, and not upon the soluble products of a saponification; but why does Mangold use *cold* alkaline permanganate if oxalic acid is not produced? However, Mr. Hehner in his literal translation admits that "the amount of oxalic acid is either not increased at all in the presence of butyric acid, or *only very slightly.*" Exactly, and by prolonged boiling one can obtain the theoretical quantity. If the fact "was not carefully suppressed to my disadvantage," it certainly at all events was not suppressed to my advantage, as time will tell.—I am, &c.,

WILLIAM JOHNSTONE.

13, Fish Street Hill,
October 24, 1891.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed

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Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxiii., No. 15, October 12, 1891.

Variation of the Composition of Jerusalem Artichokes at different Stages of their Vegetation. The part played by the Leaves.—G. Lechartier.—The author determines the composition of these plants in September when they have already reached their normal growth, and when the tubers exist only in small proportions. The leaves wither and die from the moment when they do not contain a sufficient quantity of phosphoric acid or of potassa. The minimum quantities per kilo. of dried vegetable matter are—Phosphoric acid 3·48 to 4·10 grms., potassa 3·18 to 3·36.

Circulation of the Specific Heat of Liquids.—G. Hinrichs.—The molecular specific heat of liquids at any given temperature is determined by the minimal momentum of inertia of the molecule, *i.e.*, the molecules revolve on the natural axis the momentum of inertia of which is the smallest.

Fusion-Point of Certain Binary Organic Systems.—Leo Vignon.—In all the cases examined the melting-points observed differ from the melting-points calculated. If we represent graphically the melting-points observed with reference to the variations in weight of one of the bodies composing the mixture, we have two possible cases. (*a*) The melting-points observed differ greatly from those calculated and are lower. For certain proportions of the components the mixture melts below the melting-point of the most fusible body. (*b*) The melting-points observed differ little from those calculated and are rather higher. The chemical functions of the bodies in question do not seem to affect these results.

Calorimetric Researches on the Condition of Silicon and Aluminium in Cast-Irons.—F. Osmond.—Silicon may combine with iron with disengagement of heat; but the compound formed is dissociated by an excess of iron, and subsists only if the presence of silicon in the compound is sufficient. Aluminium, in the conditions in which it is used in siderurgy, dissolves in melted iron with absorption of heat. If the reverse phenomenon is observed, as manufacturers maintain, the liberation of heat cannot be ascribed to an exothermic combination of aluminium with iron, but only to the reduction by aluminium of the dissolved iron oxide, and probably to an allotropic modification of the iron.

Formation-Heat of Platinic Bromide and of its Principal Compounds.—Léon Pigeon.—Not adapted for useful abstraction.

Zeitschrift fur Analytische Chemie. Vol. xxx., Part 3.

Separation of Cobalt and Nickel by the Nitrite Method.—M. Baubigny (*Annal. de Chemie et de Phys.*).—This method, first proposed by N. W. Fischer, is known to be excellent. It is, however, as Künzel and Erdmann have shown, not available if barium, strontium, or calcium is present, since, in this case, along with the potassium-cobalt nitrite, there is thrown down a compound of this salt with barium, strontium, or calcium nitrite. Baubigny now calls attention to a further nitrite which contains lead, nickel (nickelous oxide), and potassium. As lead salts in many respects are approximate to the barium salts it seemed to the author probable that the former would behave similarly with potassium nickelous nitrite. This conjecture was confirmed by the following experiment:—If to a solution of potassium nitrite mixed with.

nickelous acetate or nitrate there is further added only a small quantity of lead acetate or nitrate, we obtain an orange-yellow precipitate. This precipitate in appearance resembles cobalt-potassium nitrite, and is very sparingly soluble even in water acidulated with acetic acid. On qualitative examination there are found in the compound nitrous acid, lead oxide, nickelous oxide, and potassa. The presence of lead compounds, therefore, like that of the alkaline earths, excludes the use of the nitrite method for the separation of cobalt and nickel. This source of error depending on the presence of lead compounds is of the greater importance, as the alkaline nitrites are generally obtained by treating the corresponding nitrates with metallic lead, and hence often contain a small quantity of lead oxide. The nitrite to be used for the separation of cobalt and nickel must therefore always be tested for lead and purified if this metal is present. Not only cobalt and nickel, but copper, give a precipitate under the above conditions; in presence of zinc and cadmium no insoluble compounds are formed.

Solubility of Thallous Iodide and Determination of Thallium.—J. H. Long.—(From the *Journal of Analytical Chemistry*).

Determination of Cuprous Oxide in Metallic Copper by Hampe's Method.—Notes by C. Rammelsberg (*Ber. Deut. Chem. Gesell.*), Hampe (*Zeitschr. Anal. Chemie*, xvii., 127), and F. P. Dewey (*Journal of Anal. Chemistry*). It appears that on treating metallic copper with a neutral solution of silver nitrate in excess at common temperatures, all the cuprous oxide present is converted into insoluble basic nitrate, $Cu_4H_6N_2O_{12}$.

Analysis of a Mixture of Silver Chloride, Cyanide, Sulphocyanide, Ferricyanide, and Ferrocyanide.—Jules Teissier (*Bulletin de la Soc. Chimique de Paris*).—This paper will be inserted in full.

Titanium Carbide in Crude Iron.—P. W. Shimer (*Journal of Analytical Chemistry*).—The author determines titanium in irons by the following methods:—1. The residue insoluble in dilute hydrochloric acid is fused with potassium bisulphate, and the titanic acid is separated in the known manner. 2. The residue insoluble in dilute hydrochloric acid is treated with nitric acid in order to bring the titanium into solution; the nitric solution is precipitated with ammonia, the precipitate is filtered off, washed, and again dissolved in dilute sulphuric acid. After the excess of sulphuric acid has been neutralised, and the solution mixed with some sulphurous acid, the titanic acid is thrown down by prolonged boiling. The precipitate is filtered, washed, and melted with sodium carbonate. The melt, after extraction with water, yields insoluble sodium titanate, which is dissolved in sulphuric acid, and the titanic acid is finally separated from the solution. 3. The iron in the state of turnings is heated to redness in a current of dry chlorine, and the titanium chloride volatilised is received in water in a series of flasks and tubes. Of these three methods it appears that the first is preferable.

Action of Organic Compounds upon the Alkaline Sulphohydrates.—F. Fuchs (*Monat'shefte*). — Already inserted.

The Recognition of Diresorcine in Synthetic Phloroglucine.—J. Herzig and S. Zeisel (*Monat'shefte fur Chemie*).—Already inserted.

The Losses of Nitrogen in the Analysis of Guanidine and Biguanidine Compounds according to the Will-Varientrapp Method.—J. Freydl (*Monath'shefte fur Chemie*).—The author concludes that the loss of nitrogen is chiefly due to the combustion of the nitrogen formed, and that the production of cyanides has scarcely an appreciable effect.

Determination of Citric and Malic Acid in Fruits.—Edo Claassen (*Pharm. Runds.* and *Chemiker Zeitung*). The crushed fruits are stirred up with hot water, filtered, and the filtrate is mixed with milk of lime in slight excess. The liquid is acidulated with hydrochloric acid, filtered, the precipitate gently heated with an excess of ammonia until the flocculent matter which is separated out has subsided. It is then filtered off, the filtrate is evaporated to dryness, and the residue is taken up with boiling water with an addition of ammonia. The precipitate of calcium citrate is filtered off on a weighed filter and washed with hot water. The filtrate and the washings are evaporated to dryness in the same manner, and thus small quantities of calcium citrate are recovered which have become dissolved. For the determination of malic acid the crushed fruit is treated with hot water, filtered, and the filtrate is mixed with ammonia in slight excess. It is filtered again, the filtrate evaporated to dryness, and the residue finely pulverised is mixed with absolute alcohol containing ammonia. After standing for 24 hours it is filtered again, washed with absolute alcohol, and the filtrate is precipitated with an exactly sufficient quantity of an alcoholic solution of lead acetate. The precipitate of lead malate is collected on a weighed filter which has been dried at 100°, washed with alcohol, dried at 110°, and weighed. The malic acid is found on multiplying the weight of lead malate by 0·2925.

Determination of Tannin.—A number of notes from the *Journal de Pharmacie et de Chimie*, the *Chemiker Zeitung*, the CHEMICAL NEWS, the *Analyst*, *Dingler's Journal*, and the *Moniteur Scientifique*, some of which will be specially noticed by opportunity. H. M. Raer criticises in the *Journal of the American Chemical Society* the various methods for the determation of tannin. He pronounces the methods of Loewenthal and Hammer as the only useful procedures, and in these he points out certain defects.

Examination of Water; Determination of Iron.—A. F. Jolles (*Archiv. fur Hygiene*).—A colorimetric process depending on the use of ammonium sulphocyanide.

Determination of Oxygen dissolved in Water.—H. E. Roscoe and Joseph Lunt (*Ber. Deutsch. Chem. Gesell.*).—The authors point out the defects of Schützenberger's process, and propose a new apparatus by which these faults may be avoided.

Determination of Nitric Acid in Water.—G. Loof (*Pharm. Central Halle*).—The author dissolves 2 centigrms. of sodium salicylate in 5 c.c. of the water in question and adds 10 c.c. of colourless sulphuric acid, so that it may flow slowly down the side of the glass, forming 2 strata of liquid. The 2 strata are then mixed by shaking the glass, and if nitric acid is present the entire liquid takes a colour which varies from red to pale yellow, according to the proportion of the acid; 1 part of nitric acid may thus be detected in 100,000 parts of water. F. Musset states in the same paper that on testing water for nitrous acid by means of zinc iodide and starch solution with acetic acid, the reaction produced becomes continually darker and darker. This change is due to the reducing action of bacteria upon the nitrates present.

Determination of Nitric Acid.—E. Schmidt (*Apoth. Zeit.*).—This paper cannot be intelligibly reproduced without the accompanying cut.

Determination of Organic Nitrogen in Natural Waters.—T. M. Drown and H. Martin.—The authors apply the Kjeldahl process.

Colorimetric Determination of Ammonia.—Max Müller.—From the *Zeit. f. Angew. Chem.* No particulars are given.

Determination of Organic Matter in Water.—Joseph Klein (*Archiv. der Pharm.*). — A modification of the Schulze-Trommsdorff method.

Detection of Spurious Mace.—Hefelmann (*Pharm. Zeit.*).—The suspected sample is extracted with boiling alcohol and the extract filtered. If the sample is pure the filter takes up merely a faint yellow colour, but if so-called Bombay mace is present the filter is coloured red at its margin.

MISCELLANEOUS.

Edward Riley and Co.—Mr. E. Riley, F.C.S., who has been in practice as a metallurgical chemist and mineral analyst during the past thirty-seven years, has now associated himself with a duly qualified and experienced mining engineer, Mr. Frank Merricks, Associate Royal School of Mines, &c., also an experienced analyst and metallurgist. Mr. W. H. Heidsman, who has been associated with Mr. Riley for the past twenty years, and has had considerable mining and metallurgical experience in all parts of Europe, will assume the management of this branch of the business, and will assist in carrying on the metallurgical and analytical business as heretofore. A branch office will be opened immediately in Cordova, Spain, under the charge of Mr. Merricks. The firm will be prepared to undertake the inspection of mining properties of all kinds in Spain or elsewhere, and to advise and superintend prospecting work, and all smelting, refining, and other metallurgical operations.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Laboratory without Gas.—Would any chemist who has practical experience on the subject oblige by informing me as to the best means of carrying on the work of a small laboratory in a district where there is no gas ?—F.I.C.

Manufacture of Soap.—Will you oblige one of your subscribers by letting me know what are the latest books treating of manufacture of soap in England, with the name and address of the publishers ?—H. MANBERT.

[The following books may be consulted on the manufacture of soap:—"On the Manufacture of Soaps," by C. Morfit (1871); Trübner and Co., London. "Soaps and Candles," by James Cameron (1888); J. and A. Churchill, London. "Soap, Candles, Lubricants, and Glycerin," by W. L. Carpenter (1885); E. and F. N. Spon, London. "The Art of Soap-making," by A. Watt (1885); Crosby Lockwood and Co., London.—Ed. C. N.]

MEETINGS FOR THE WEEK.

MONDAY, Nov. 2nd.—Royal Institution, 5. General Monthly Meeting.
THURSDAY, 5th.—Chemical, 8.
FRIDAY, 6th.— Physical, 5. "On Corresponding Temperatures Pressures, and Volumes," by Prof. Sydney Young.

ERRATUM.—P. 204, col. 2, line 26 from bottom, *for* "*Analyst,* October. 1891," *read* "*Analyst,* September, 1891, p. 169."

THE CHEMICAL NEWS

AND
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VOL. LXIV., No. 1667.

ELECTROLYTIC DETERMINATION OF METALS AS AMALGAMS.*

By G. VORTMANN.

IN the determination of metals by the electrolysis of their solutions it is essential in the first place for the metal to be separated out quantitatively as such or in the state of a known compound, and secondly that the precipitate obtained forms a uniform coating on the platinum capsule used as an electrode, and adheres so firmly that no loss takes place on rinsing with water and alcohol and undergoes no change during drying. Among the metals which have been hitherto determined electrolytically iron, cobalt, nickel, zinc, cadmium, bismuth, copper, mercury, silver, gold, platinum, tin, and antimony have been separated as metals, but manganese and lead as peroxides. Some of the metals above-mentioned present difficulties in electrolysis, as they form a uniform adhesive stratum only if present in small quantities, such as antimony, bismuth, cadmium, lead, and manganese. The idea of obtaining a uniform adhesive coating by the addition of such metals as are apt to be deposited as spongy masses seems first to have presented itself to C. Luckow, who in 1880 observed the formation of amalgams on the simultaneous deposition of mercury and of other metals. In 1885 he gave directions for obtaining zinc as an amalgam, and recommended an addition of mercury for the separation of silver from the solution of its nitrate. Before Luckow, W. Gibbs (1883) recommended to place a weighed quantity of mercury upon the bottom of the beaker containing the solution of the metal connecting it with the negative pole of the battery. The quantity of the metal deposited was to be concluded from the increase in the weight of the mercury. Gibbs employed this method for the determination of mercury, cobalt, and tin, and regarded it as probably not applicable to antimony and arsenic. Strictly speaking, he merely intended to use mercury as a negative electrode in place of the platinum capsule.

In view of the practical importance and the convenience of the electrolytic methods, I considered it advisable to attempt the separation of all those metals in the form of amalgams which have hitherto been electrolytically determinable only with especial precautions. I used the mercury not in the metallic state, but preferred mercury chloride, which is more easily weighed and obtained in a pure condition, or, in its place, in the electrolysis of acid solutions I used pure mercuric oxide obtained by precipitation. In the simultaneous separation of mercury along with the metal to be determined, the amalgam is more uniformly deposited than if metallic mercury had been used. The precipitability of mercury from all its solutions much assists the determination of metals as amalgams. It is sufficiently known that it can be readily deposited from acid solutions, from its solution in potassium cyanide, and from the solution of the double sodium pyrophosphate after the addition of ammonia or ammonium carbonate. It may also be easily separated from the solution of the double ammonium oxalate, from the solution of its salts in potassium iodide, in sodium sulphide, or in ammonia in presence of tartaric acid.

All the precipitates after the completion of the electrolysis were washed first with water, then with alcohol, and lastly with ether, dried, and gently blowing upon it, whilst the capsule is gently warmed by holding it in the

palm of the hand and finally placing it in the desiccator. It is not necessary to weigh the amalgams forthwith, as no loss takes place by volatilisation of mercury if the capsule is left for days in the desiccator or even in the open air.

The strength of the current the author regulated entirely according to the progress of the analysis. At the beginning of the electrolysis a current was passed for some minutes, giving 6—8 c.c. detonating gas per minute; as soon as the metals began to be separated the current was reduced to 2—3 c.c. of gas per minute, and again strengthened gradually, so that the analysis was generally completed with a current giving 6—8 c.c. of detonating gas per minute.

Determination of Mercury.

1. *Separation of Mercury from the Solution of Ammonium Oxalate.*—If a solution of mercuric chloride is mixed with ammonium oxalate in excess it remains clear, and on electrolysis the mercury is readily separated. This method, like the separation of mercuric chloride from an acid solution, has the defect that a thin film of calomel is formed on the surface of the liquid, which is reduced only after a long time.

2. *Separation of Mercury from an Ammoniacal Solution.*—The solution of mercuric chloride in water is mixed with tartaric acid, ammonia in excess is then added, and the liquid is then electrolysed. The mercury separates well and quickly by this process : ammonium sulphide is used to ascertain if the precipitation is complete.

3. *Separation of Mercury from a Solution of Sodium Sulphide.*—Mercuric chloride is dissolved in water and mixed with a solution of sodium hydroxide containing sodium sulphide until the precipitate first formed is completely re-dissolved. The liquid is then diluted with water and the electric current is passed through. The solution of the mercurial salt in sodium sulphide is not always clear ; sometimes a slight turbidity is perceptible, probably due to finely-divided metallic mercury, but which does not interfere with the electrolysis. The separation of the mercury ensues easily and completely, and it is at an end when a specimen of the solution remains clear on adding ammonium chloride. At the commencement of the electrolysis the positive electrode becomes overcast with a black film of mercury sulphide which gradually disappears again. As a rule the separation of mercury is complete when the positive electrode is covered with a yellow layer of sulphur and the black film has disappeared.

The mercury separated from the solution of sodium sulphide coats the capsule uniformly as a reflective layer, consisting in part of minute drops.

4. *Separation of Mercury from Solution of Potassium Iodide.*—On the electrolysis of a solution of mercuric chloride in an excess of potassium iodide the mercury separates easily and uniformly, whilst iodine is liberated at the positive pole and finally floats on the surface of the liquid in the form of a cellulose clot. If a specimen of the liquid after being decolorised with sodium sulphide is not coloured brown on the addition of ammonium sulphide all the mercury has been separated out.

A few c.c. of concentrated soda-lye is then poured into the capsule without interrupting the current, the liquid is mixed by moving the positive electrode up and down until the iodine is completely dissolved, and the current, slightly strengthened, is passed through the liquid for an hour in order to re-precipitate any traces of mercury which have been re-dissolved by contact with the solid iodine. If a sample of the solution on the addition of ammonium sulphide gives a pure white milky precipitate, the alkaline liquid is poured off, and the mercury is washed in the manner described above. If the quantity of iodine liberated is small, the iodiferous solution is poured off and the mercury quickly washed first with solution of sodium sulphite and then with water, alcohol, and ether.

The solution of the mercuric chloride can be mixed to

any extent with soda- or potassa-lye without causing a precipitate. From such an alkaline solution the mercury may be readily deposited electrolytically and washed with pure water only, as on rinsing with alcohol, small quantities pass into solution in the state of a grey film. E. F. Smith has observed a similar fact in mercury separated from a solution of potassium cyanide.

The mercury precipitated electrolytically in any manner is permanent in the air and undergoes no change on remaining 15 hours in the desiccator.

(To be continued).

ELECTROLYTIC SEPARATIONS.

By EDGAR F. SMITH and F. MUHR.

As it appeared from the author's former experiments (*Amer. Chem. Jour.*, xii., p. 252) that gold can be completely precipitated by the electric current from its double cyanides, the author attempted to decide what metals can be separated from gold in this manner. Former experiments had showed that in a current of 1-100th ampère requires 36 hours to separate palladium from a solution containing potassium cyanide in excess. This behaviour indicated the possibility of separating gold from palladium, and the two metals were therefore submitted to the current under the following condition :—0·1162 grm. gold and 0·1200 grm. palladium dissolved in 1½ grms. potassium cyanide and made up to 150 c.c. were treated with a current giving off 0·8 c.c. of detonating gas per minute. The quantity of gold obtained was 0·1162 grm. The separation of the gold required 12—14 hours. Water both cold and warm was used for washing the precipitated metal, and the deposits were produced at once in the platinum capsules.

The gold was then dissolved by pouring a dilute solution of potassium cyanide into the platinum vessels and separated by connecting the latter with the anode of a weak battery.

The solution of gold cyanide was decomposed by aqua regia, and the gold chloride obtained was carefully tested for palladium. But no palladium was discovered.

Gold from Copper.—This separation was found successful. 0·1725 grm. gold and 0·1250 grm. copper dissolved in 1¼ grms. potassium cyanide and made up to 150 c.c. were submitted for 12—14 hours to a current giving off 0·8 c.c. detonating gas per minute. The quantity of gold obtained was 0·1725 grm., and no copper was found in the deposit.

Gold from Cobalt.—The quantities taken for the experiment were 0·1792 grm. gold and 0·15—0·20 cobalt were dissolved in 3 grms. potassium cyanide, diluted to 150 c.c., and treated with a current giving only 0·6 c.c. gas per minute. The gold found was 0·1789 grm.

Gold and Nickel.—The quantities taken were gold 0·1725 grm., nickel 0·1373 grm. in potassium cyanide, made up to 150 c.c. and submitted to a current of 0·5 c.c. per minute. The gold extracted was 0·1724 grm.

The electrolytic separation of zinc from mercury, cadmium, and silver, in a solution of potassium cyanide, was effected without difficulty, but the current must yield at least 2—3 c.c. of detonating gas per minute.

Gold from Zinc.—The quantities taken were 0·1792 gold, 0·2 zinc, potassium cyanide 3 grms., made up to 150 c.c. and treated with a current giving 0·5 c.c. of detonating gas per minute. The amount of gold found was 0·1796 grm. The battery used consisted of 5—10 "crow-foot cells." The poles during the precipitation of the metals were at a distance of 1½ inches from each other. The solutions were covered with watch-glasses to prevent loss and exclude dust. The precipitation of the metal is completed as soon as the surface of a sheet of platinum freshly introduced remains unaltered.

Gold from Platinum.—For this separation a more powerful current was used. The quantities taken were 0·1467 grm. gold, 0·2433 grm. platinum, in potassium cyanide 2¼ grms., made up to 150 c.c. The current gave off 1 c.c. detonating gas per minute. The gold obtained was 0·1474 grm.

Silver from Platinum.—The metals were dissolved in an excess of potassium cyanide, and the solution was directly electrolysed, using a current of the same strength as that in the last experiment. The silver was deposited free from platinum.

Cadmium from Platinum.—The cadmium precipitated was never free from platinum.

Mercury from Platinum.—This separation is easily effected. For quantities of mercury 0·1902 grm., and platinum 0·2433, a current was used giving off only 0·2 c.c. of gas per minute. The mercury found was 0·190 grm. The separations of gold, silver, and mercury from platinum were effected in the cold.—*Ber. Deut. Chem. Gesell.*, vol. xxiv., p. 2175.

DETERMINATION OF SMALL QUANTITIES OF ALKALI AND RECOGNITION OF THE NEUTRALITY OF WATER.

By F. MYLIUS and F. FOERSTER.

A CERTAIN conclusion as to the insolubility of glass vessels in aqueous liquids has been hitherto involved in considerable difficulties, as the only available means has been a determination of the loss of weight which the vessels underwent on being heated with such liquids. We have sought to determine the permanence of glasses by the direct determination of the quantity of alkali dissolved out of them by water. It was evident that, in order to obtain more precise results, the gravimetrical method must be superseded by a volumetrical procedure. The necessary increase of the sensitiveness of alkali-methods has been attained by means of a special indicator (iodeosine), which one of us had already proposed for the comparative examination of the surfaces of glasses.

Each of the colouring-matters used in volumetric analysis as indicators has a special value, and is adapted to a given purpose. The sensitiveness of indicators is in every case limited, as in titration with very dilute solutions the change of colour is only effected gradually. The cause of this lies especially in the hydrolytic scission to which the salts of tinctorial acids are liable in dilute solutions. Hence near the neutral point the colour of the free tinctorial acid appears along with the colour of the salt when the acid is coloured, or if it is colourless the colour of the salt fades away, but in neither case do we encounter an abrupt change of colour. For the titration of dilute solutions such indicators are preferable as, like the strong acids, form the most permanent alkaline salts. Titration with them is little affected by the presence of carbonic acid, since, being powerful acids, they easily expel carbonic acid from carbonates.

Among the artificial colours which have recently come into use these properties seem to a great degree characteristic of the eosines, as their halogenous power probably depends on their high proportion of halogen. Their fundamental substance, fluoresceine, as also ordinary eosine, has been introduced into volumetric practice. Our experiments have shown that iodeosine, or erythrosine, is especially adapted for the determination of small quantities, but under peculiar conditions, which render a preliminary investigation of its properties necessary.

Iodeosine, or erythrosine, has the composition $C_{20}H_8I_4O_5$; it is a commercial product, and is especially used in cotton-dyeing and paper-staining.

The pigment, as supplied by the Baden Aniline Works is a brick-red powder, soluble without fluorescence, but

with a rose-colour in dilute alkalies. From this solution it is re-precipitated by supersaturation with acid. The commercial preparation contains as impurity small quantities of matters almost insoluble in ether and in dilute solution of pyridine. The alkaline solution of these impurities has a violet-blue tone. For its purification the commercial substance was dissolved in aqueous ether, and removed from the filtered solution by shaking out with a dilute soda-lye; from the alkaline solution the brick-red sodium salt is precipitated by a stronger soda-lye. The salt is filtered, washed with spirit, and re-crystallised from hot alcohol. As the solution cools it is obtained in well-developed, almost rectangular tables, with a green surface colour, whilst the impurities remain in the mother-liquor.

Pure iodeosine has a decidedly lighter colour than the commercial product; it is almost insoluble in absolute ether, benzene, petroleum ether, chloroform; more readily soluble in acetone, in alcohol, and in aqueous ether. In aqueous alkali the purified colouring-matter dissolves, as it might be expected, with a more yellowish tone than the crude product. Supersaturated solutions can be obtained by shaking up the recently precipitated amorphous colouring-matter with ether. If the solution is allowed to stand, the excess of colour is deposited in small orange crystals of a rhombic form.

Iodeosine has not hitherto been employed in alkalimetry; if it is used in the ordinary manner it behaves as a bad indicator. If to an alkaline solution we add a trace of iodeosine, and neutralise with normal hydrochloric acid, the change from rose to orange takes place with undesirable tardiness, and a decided excess of acid is necessary to complete the reaction. The use of this colour as an indicator is possible only if the titration is effected in presence of ether in a shaking vessel. The neutral point can then be distinguished very sharply, as the slightest excess of acid on shaking causes the trace of eosine present to pass from the aqueous into the ethereal stratum. The aqueous liquid then appears colourless.

Titration with Mille-Normal Solutions.

In the determination of large quantities of alkali, effected with normal and decinormal solutions, there is no cause to make use of the process just mentioned, the employment of the ordinary indicators in aqueous solutions being then more convenient. In the ordinary manner we may, as is well known, effect titrations with centinormal solutions with some accuracy. But this is the limit. By means of iodeosine and ether it is possible to effect titrations with mille-normal solutions with the greatest distinctness.

(To be continued.)

PROPERTIES OF PRECIPITATES, &c.*

By E. WALLER, Ph.D.

(Continued from p. 220).

$Fe_2(OH)_6$.

Rem.—Precipitation in most cases effected by NH_4OH.

When but little ferrous iron is present and heat is applied, a finely-divided red (" brick-dust ") precipitate separates, which is insoluble except in concentrated HCl.

In presence of a larger proportion of ferrous salt, black $Fe_3(OH)_8 = Fe(OH)_2, Fe_2(OH)_6$ will separate. With more ferrous salt the precipitate is green, the colour being lighter the larger the proportion of ferrous salt; and when the iron is all absolutely in the ferrous form, the precipitate is white. Whenever ferrous salt is present, a double ammonium ferrous salt forms, which remains in solution, from which the iron slowly precipitates by

* From *School of Mines Quarterly*, xii., No. 3.

absorption of oxygen and conversion to the ferric form. NH_4Cl favours the precipitation of $Fe_2(OH)_6$.

Cond.—Iron should be in ferric form. H_2S should be absent.

Sol.—Soluble in acids and in solution containing citric, tartaric acids, &c., as well as other organic substances, glycerin, sugar, &c. Insoluble in alkalies.

Contam.—Basic ferric salts, especially basic sulphate, unless the precipitant is in moderate excess. When precipitated by fixed alkalies the precipitate contains some alkali, which is washed out with great difficulty. Precipitate will carry with it phosphoric acid as $Fe_2(PO_4)_2$ in nearly sufficient quantity to form that compound. The excess of phosphoric acid will remain in solution unless some other base (Al, Ca, &c.) is present to carry it down in combination. Precipitate may also contain nearly, if not quite, all of the Al, Mn, and silica present. Mg, Co, Ni, Zn, and Cu are also liable to be present in the precipitate, Ca also as $CaCO_3$ if the alkaline solution has absorbed any CO_2 from the atmosphere. From these latter (Mg, &c., including Ca), the precipitate may be freed by one or more re-solutions and re-precipitations.

Ign.—Converted to Fe_2O_3. With C, a partial reduction to Fe_3O_4 may occur. Fe_2O_3 is restored by adding a few drops of HNO_3, and re-ignition. In contact with NH_4Cl, may form volatile Fe_2Cl_6.

$Fe_2(OH)_n(C_2H_3O_2)_{6-n}$. Basic Ferric Acetate.

Rem.—Ferrous salts, if present, are not precipitated. If in very small proportion, they may induce the formation of the " brick-dust " precipitate alluded to under $Fe_2(OH)_6$. In analysis of iron ores and manufactured irons, the reduction of the major part of the iron to the ferrous form and application of the basic acetate, separation is frequently resorted to in order to remove the excess of iron before determining phosphorus.

Cond.—The *dilute* solution should contain but little free acetic acid. The (ferric) iron should be in the form of acetate. This is obtained by neutralising the free mineral acid present and adding $NaC_2H_3O_2$. No precipitate should appear in the cold, but on boiling a few minutes (three to five) it separates completely, provided not too much free acetic acid is present. *Too long boiling* causes the precipitate to assume a form which filters with some difficulty.

Sol.—Soluble in cold dilute acetic acid and in mineral acids, also in citrates and other organic substances mentioned as solvents of $Fe_2(OH)_6$. Insoluble in hot acetic acid only when quite dilute.

Contam.—Salts of fixed alkalies. Silica, alumina salts, and P_2O_5,—the latter in the form of $Fe_2(PO_4)_2$ [see $Fe_2(OH)_6$]. The precipitate may also contain some Mn, Zn, Ni, Co, or Cu. Mn is more likely to be present if the amount of $NaC_2H_3O_2$ added was large. The amounts of these last in the precipitate is much diminished by increasing the proportion of free acetic acid in the solution. The danger of having sufficient free acid to prevent the precipitation of all the iron is, however, considerable. By re-dissolving in HCl, neutralising, adding $NaC_2H_3O_2$ and re-precipitating, the Zn, Ni, &c., can be removed. Zn usually gives the most trouble. If much is present, it may be advisable to precipitate in a solution containing enough free (acetic) acid to hold a little Fe in solution. The later may be separated by evaporating the excess of acid from the filtrate. SiO_2 and Cu should be previously removed by known methods, if their presence in the precipitate will influence subsequent work.

When chromium is present in the solution the action is peculiar. When iron predominates decidedly, all of the chromium is precipitated with it. If the ratio of chromium to iron is nearly the same, not only much of the chromium, but some of the iron is retained in the solution.

$Al_2(OH)_6$.

Rem.—In general terms the precipitate is very similar to $Fe_2(OH)_6$, but is more easily prevented from forming,

and when separated, being more gelatinous in character, is less readily managed. Usual precipitate ammonia. A good method of managing consists in rendering slightly alkaline with ammonia, and passing H_2S, raising the temperature at the same time gradually to boiling.

Cond.—Neutral or slightly alkaline solution, containing preferably NH_4Cl.

Sol.—Dissolves in acids and in fixed caustic alkalies; somewhat soluble in ammonia, especially in the cold. From this solution it may be separated by boiling out the major part of the NH_3, particularly if NH_4Cl is present. Precipitation prevented by presence of tartrates, citrates, sugar, glycerin, &c. After boiling or standing for a short time the precipitate will dissolve in acids (even HCl) slowly and with some difficulty.

Contam.—Basic Al salts, especially the sulphate. Retains P_2O_5 in proportion sufficient to form $Al_2(PO_4)_2$. May also contain Fe, Mn, or SiO_2 (hydrated). Possibly also Mg, Zn, Co, Ni, Cu, &c., from which last it may be freed by re-solution and re-precipitation except, perhaps, in the case of Zn, from which a complete separation of $Al_2(OH)_6$ can scarcely be effected. Ca may also accompany it as $CaCO_3$ if the alkaline solution has absorbed CO_2.

Ign.—Converted to Al_2O_3. Ignited with NH_4Cl some volatile Al_2Cl_6 may form. After ignition practically insoluble in HCl. Converted to a soluble form by fusion with an alkaline flux.

$Al_2(PO_4)_2$.
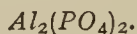
Rem.—Of service in the determination of Al in manufactured irons and in mineral phosphates.

Cond.—Fe, if present, should be in the ferrous form. The conditions usually produced are a solution acid with acetic, in which Fe has been reduced by $Na_2S_2O_3$, and containing an excess of alkaline phosphate. This is boiled for some time.

Sol.—Dissolves in mineral acids. Insoluble in moderately strong $HC_2H_3O_2$. Prevented by tartrates, citrates, &c., in the same way as $Al_2(OH)_6$.

Contam.—$Fe_2(PO_4)_2$ and possibly basic ferric salt. If Fe is kept entirely in the ferrous condition (which is not always possible), this contamination would not occur. Remedied by re-dissolving, reducing, and re-precipitating. $Ca_3(PO_4)_2$ (or alkaline salts if the solution is not sufficiently dilute), may also accompany the precipitate. Remedy by re-solution and re-precipitation. Glaser's method for mineral phosphates involves the previous separation of the lime, as $CaSO_4$, by the aid of alcohol (*Zeit. Angew. Chemie*, 1889, p. 636).

$Al_2(OH)_n(C_2H_3O_2)_{6-n}$. *Basic Alumina Acetate.*
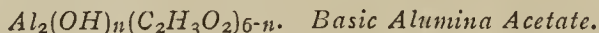
Rem.—Very similar to the corresponding Fe compound. Being more slimy in character, it gives more trouble in filtering and general management. Used for separation only.

Cond.—The same as for the Fe compound. Practically no free acetic acid is admissible. Al should be in the form of acetate. Precipitate obtained by boiling. If boiled too long it filters and washes with more difficulty.

Sol.—Dissolves in acids to some extent in very dilute boiling acetic. If the solution after boiling is allowed to cool, a considerable proportion re-dissolves. Soluble, or precipitation prevented by citrates, tartrates, &c. The small amount almost invariably remaining in the filtrate may be recovered by careful neutralisation and boiling, or better by evaporating to dryness and taking up with dilute acetic.

Contam.—As for the Fe compound. Salts of fixed alkalies, P_2O_5 [in proportion sufficient to form $Al_2(PO_4)_2$)] SiO_2 (hydrated), Mn, Zn, &c.

$Cr_2(OH)_6$.
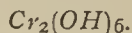
Rem.—In general properties this precipitate resembles $Al_2(OH)_6$, and its management is similar. Its tendency to carry with it other substances requires that it shall

always be re-dissolved and re-precipitated with ammonia at least twice.

Cond.—Absence of members of $(NH_4)_2S$ groups, and preferably of all non-volatile salts. Solution must be exactly neutral (ammonia added in slight excess and then boiled until neutral). NH_4Cl assists the separation.

Sol.—Dissolves in all acids, in fixed alkaline hydrates, and perceptibly in excess of NH_4OH. Soluble or prevented from precipitating by tartrates, citrates, sugar, &c.

Contam.—Salts of fixed alkalies, alkaline earths, members of the $(NH_4)_2$ S group, &c. (See above, *Rem.*)

Ign.—Converted to Cr_2O_3, in which form, if strongly ignited, it becomes insoluble in HCl. In presence of fixed alkalies or alkaline salts and in contact with the oxygen of the air, is partially or entirely converted to chromate.

(To be continued).

ON THE OCCURRENCE OF NITROGEN IN URANINITE, AND ON THE COMPOSITION OF URANINITE IN GENERAL.*

By W. F. HILLEBRAND.

(Continued from p. 222.)

Methods of Analysis.

ORDINARILY not less than 2 grms. was taken for the main analysis. Solution was effected in the least possible quantity of weak nitric acid at the temperature of the water-bath, so as to dissolve as little of the gangue as possible. When disengagement of gas bubbles had entirely ceased the uranite was decomposed. Any black powder then remaining was treated as gangue, being columbite. The gaseous products of decomposition of the nitric acid are but faintly reddish. After filtering, the insoluble matter was ignited and weighed. A necessary refinement, in cases where the amount of gangue is appreciable, is to weigh it at 100° C., and then to ascertain how much, if any, water it contains. The filtrate was evaporated to dryness in platinum to obtain soluble silica, which after weighing was tested as to purity by hydrofluoric and sulphuric acids. From the filtrate lead was thrown down by hydrogen sulphide, and weighed eventually as sulphate. Iron and manganese were then removed as sulphides, while the earths and uranium were held in solution by ammonium carbonate and ammonia. This was effected in a flask of not over 250 c.m.³ capacity, in which the precipitate was allowed to settle over night. A precaution to be observed is to add ammonia as well as ammonium carbonate, otherwise the earths thrown down with uranium on neutralisation of the originally acid solution will be only partially re-dissolved. In order to ascertain this it is best to remove the hydrogen sulphide from the filtrate from lead sulphide before proceeding to the precipitation of iron. On adding ammonia and ammonium carbonate it can then be readily seen when the earths are dissolved, which is not at all easy if the hydrogen sulphide has not been first expelled. Calcium could rarely be found with the iron. The sulphide precipitate and the filter were roasted and weighed as a check, and then iron was separated from manganese if necessary, and the amount of the former determined as Fe_2O_3, which was generally checked by re-solution, reduction by hydrogen, and titration by potassium permanganate.

If any doubt had existed as to the completeness of separation from the earths, the iron and manganese were a second time precipitated as sulphides in the presence of ammonia and ammonium carbonate.

The filtrate or filtrates, as the case might be, were

gently heated till all ammonium carbonate was driven off, the precipitate was dissolved in nitric acid, and separation of earths and uranium from any traces of magnesia and alkalies present effected by freshly prepared ammonium sulphide, allowing to digest for an hour in a covered platinum dish on the water-bath. As others have experienced, it was found that no separation from calcium can be effected by this method. While this element was always present in small quantity, it could very rarely be detected in the filtrate. Nevertheless the above method was preferred to that of Alibegoff (*Ann. d. Chem.*, 1886, vol. ccxxxiii., p. 133), in which uranium is separated from alkaline earths, magnesium, and alkalies by mercuric oxide, because of the necessity of converting the nitrates into chlorides for the success of the latter operation, whereby an additional reagent is employed and the manipulations are increased, both of which it was desired to reduce to a minimum.

From the precipitate of earths and uranous oxide mixed with sulphur, the oxides were extracted by nitric acid, the solution was evaporated to dryness, water was added, and then, when boiling, oxalic acid and two or three drops of ammonium oxalate. The precipitated oxalates were washed in due time with weak oxalic acid solution, ignited, and preserved in the crucible till later. The filtrate, which still always contains some rare earth metals and calcium, was evaporated to dryness, ignited to destroy oxalates, re-dissolved in nitric acid, and evaporated with sulphuric acid in quantity slightly more than sufficient to convert into sulphates. After removal of all nitric acid the residue was dissolved in a little water, and two and a half to three times the bulk of alcohol was added. In the course of twelve hours or more the precipitate, containing all the calcium not originally thrown down by oxalic acid, besides some sulphates of the rare earths, was collected on a filter, washed with alcohol, dried, dissolved in weak nitric acid, and the rare earths were separated from calcium by ammonia and weighed with the main portion.

The alcoholic filtrate was evaporated to dryness, ignited, dissolved in nitric acid, and the precipitate produced by boiling with ammonia was ignited repeatedly in air and in hydrogen until a constant weight was reached by reduction. The UO_2 thus obtained was apparently never entirely free from rare earths, amounting usually to a quarter or a third of a per cent of the mineral. They were in two analyses recovered by treating the perfectly dried nitrates with ether, filtering, washing with ether, dissolving the insoluble nitrates of the earths and some uranium in water acidulated with a drop of nitric acid, and then adding oxalic acid to the hot aqueous solution after evaporating to dryness. The earths were weighed with the already tared main portion, and a proper deduction was made from the uranium oxide. It is best always to make a second precipitation by ether to insure extracting the last traces of earths from the uranium.

The earths as weighed contain the balance of the calcium and a small quantity of uranium. Solution was effected by prolonged digestion with sulphuric acid somewhat diluted, repeated after filtration if necessary. Thorium, cerium, lanthanum, and didymium were then separated from the yttrium earths by potassium sulphate in as nearly neutral a solution as could be obtained. Thorium and cerium were separated from lanthanum and didymium by long passage of chlorine gas through a solution of sodium hydrate holding the gelatinous hydrates of the earths in suspension. Finally, thorium was separated from cerium by boiling with sodium hyposulphite. Small quantities of what might be zirconia were now and then found, but its identity could not be proved.[*] The turmeric paper test for this element has never proved of any value in my hands where small amounts of it were present. The earths of the yttrium

group and the uranium were precipitated from the potassium sulphate solution by ammonia, re-dissolved in nitric acid, the solution was evaporated to dryness, and the earths were precipitated from aqueous solution by oxalic acid and weighed, after which they were examined for calcium, as was also the filtrate from them containing the uranium and that containing the potassium sulphate, in both of which calcium might be found. The combined calcium oxide was deducted from the original weight of the earths and added to the lime earlier separated by alcohol. The small amount of uranium recovered— usually 4 to 7 m.grms. as UO_2—was likewise deducted from the earths and added to the main portion.

In the last analysis of Glastonbury uraninite, which was made especially with a view to great accuracy in summation, and in Analysis XVIII., a modification was introduced at one point which is perhaps worthy of retention in future work. Instead of evaporating the filtrate from iron sulphide to complete removal of ammonium carbonate, the gradually forming precipitate of carbonates was removed by filtration at a point where the earth carbonates are almost entirely thrown out and the uranium is still in solution. A little practice enables one to recognise this point readily. When the filtrate is treated as already described in the first method, oxalic acid will generally fail to show any earths present with the uranium, but the precipitation by alcohol, and later by ether, must not be neglected. The carbonates are now dissolved in nitric acid, the solution is evaporated to dryness, and the rare earths are separated by oxalic acid in perfect purity, except perhaps for a little lime, from the small amount of uranium they contain. The resulting filtrate will always contain a little of the earths, for it has been my experience that the precipitation by oxalic acid is never absolute. It is best to unite it with the main portion of uranium and separate lime and some of the earths at the proper stage by alcohol, and from the weighed UO_2 the remainder of the earths by ether. So far as my limited experience with this modification goes it has proved satisfactory and decidedly preferable to the procedure first given, the chief point gained being that a purification of the earths from uranium is unnecessary and the trustworthiness of the weight found for the combined earths is heightened.

It may be said, as regards the purity of the different earths or groups of earths after separation, that, whereas the original ignited mixture was somewhat dark, without sharply characterisable colour tint, the thoria was pure white and gave the theoretical molecular weight; the ceric oxide dissolved with a strong yellow colour in concentrated sulphuric acid, which was bleached instantly by sulphurous acid, and with lead peroxide and nitric acid it gave likewise a deep yellow colour; the lanthanum and didymium were cinnamon-brown in colour, soluble in weak nitric acid, and the gelatinous precipitate by ammonia from acetic solution gave sometimes a blue colour with powdered iodine, due to lanthanum; the yttrium earths were pale straw-coloured, and dissolved very readily in weak acids. Although only a single separation of the yttrium group by potassium sulphate was made, it was probably nearly perfect, for any remainder should have been obtained subsequently with the lanthanum and didymium, and the quantity of these was so small as to preclude much contamination by earths of the yttrium group.

Concerning the estimation of magnesia and alkalies, and traces of phosphoric acid, nothing need be said.

Water was estimated by heating the mineral in a current of air and collecting the water in a calcium chloride tube. In only one case—the last Glastonbury analysis—was the mineral fused in a boat with sodium carbonate in order to retain the substance or substances which imparted to the water expelled by simple ignition an acid reaction. The weight of water found was hereby slightly reduced, and perhaps a similar result would have followed the taking of a like precaution in other cases.

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[*] Except in the Colorado uranite, which contains practically no other earths than zirconia.

The acid property of the water was perhaps due to fluorine, since a trace was found in the Glastonbury mineral, but by no means enough to account for even the slight difference observed between the gains of the absorption tube by the two modes of ignition.

The correct estimation of UO_2 is of the utmost importance, and it was in consequence of remarkable variations in results first obtained that much material, which would have been of inestimable value at a later period, was used up in endeavours to secure concordance. An obvious source of error at first was the formation, in the sealed tubes in which decomposition of the mineral with rather strong sulphuric acid was effected, of bright green crystals of a thorium-uranous sulphate which were almost insoluble in water, and hence necessitated such a length of time for titration as to seriously discredit the results. Dilution of the acid proved a remedy for this difficulty, and perfectly satisfactory solution* was obtained with one volume of concentrated sulphuric acid to six volumes of water. This proportion was employed in all subsequent work by this method, and decomposition of the uraninite was generally complete by leaving the tubes in an air-bath over night at a temperature of 150° to 175° C. The end reaction with potassium permanganate was then always sharp and satisfactory, but the results were still discordant. The cause was eventually found to be in the manner in which the tubes were filled with carbon dioxide. This was done by introducing either solid sodium carbonate or a solution of the same, and sealing as quickly as possible. It is, however, almost impossible to prevent access of air, often in considerable amount, through the drawn-out neck of the tube before the seal can be made. The following figures are the results of titration on one sample of Glastonbury uraninite. They are tolerably concordant compared with other series, and yet are undoubtedly one and all too low UO_2 found 55·00, 54·12, 56·98, 55·93, 56·15, 55·61. Every now and then a result would fall so far below all others of a series as to be positively startling.

When, however, the tubes were filled with carbonic acid from an external generator through a fine glass tube drawn out of the same kind of glass as that of which the decomposing tube consisted, and the fine tube was sealed into the other while the gas continued to pass, all air except the trace in the carbonic acid itself was excluded, and after decomposition the titration results showed a concordance and accuracy that could not be surpassed, as shown by the following series made on carefully purified U_3O_8, using freshly boiled distilled water :—

UO_2 found 32·11, 31·90, 32·15, 32·12, 32·06, 32·17, 32·28.
Theory requires 32·07.

That it is immaterial whether the water is free from oxygen or has stood for some days exposed to the air is shown by the following series, in which water several days old was used :—

UO_2 found 32·11, 31·85, 32·37, 32·36, 32·13.

An excess over theory is to be expected, for it is difficult to prepare U_3O_8 with the theoretical percentage of UO_2.

In order to test the probable error of previous titrations the following determinations were made, in which the tube was filled as carefully as possible with carbonic acid by using a solution of sodium carbonate :—

* Although the green crystals were no longer formed, there still appeared, as when stronger acid was used, a curious crystallisation, taking the form of excessively fine needles woven into a felt-like mass which covered the surface of the liquid from end to end of the tube, and when put in motion by a movement of the solution resembled an undulating white rope. This was readily soluble in water, and did not affect the titration at all, but it was observed on a few occasions, when the heating of the tubes was continued for several days, that it gradually disappeared, and in its place an abundant crop of unusually large and clear green crystals was formed. Of the latter, 0·5209 grm. gave on analysis :—UO_2 49·53, ThO_2 3·61, SO_3 32·32, H_2O 13·59; total, 99·05 ; whence is derived the molecular ratio $UO_2(ThO_2):SO_3:H_2O$ as 1:2·06:3·04, and the formula $(UTh)O_4(SO_2)_2, 4H_2O$. Being formed from a much more dilute acid they may possibly differ from the crystals deposited from strong acid in the number of molecules of water. It is intended to make a more thorough examination of this salt at some future time.

UO_2 found 31·06, 31·07, 29·72, 29·33, 29·89, 30·69.
Theory requires 32·07.

Two out of the three experiments by Zimmerman (*Ann. d. Chem.*, 1886, ccxxxii., 287, lines 5 and 6)), in which UO_2 in U_3O_8 was estimated by permanganate after solution by hydrochloric acid in sealed tubes, using manganese sulphate to counteract the effect of the acid, gave 31·39 UO_2 instead of 32·07.

Finally a set of tests was made on a specimen of North Carolina uraninite in order to ascertain the degree of concordance to be reached on the mineral.

UO_2 found 38·14, 38·12, 38·12, 38·04, 38·07, 37·97, 37·87. Solution in the last two cases had been effected at 100° C., and was, perhaps, not quite perfect.

It is thus apparent that, with due regard to the exclusion of all air from the tube, the method leaves nothing to be desired as regards accuracy. The acid employed was specially distilled, and gave with brucine and diphenylamine no indication of nitric acid, the test being made as prescribed by Wagner (*Zeit. f. Anal. Chem.*, 1881, p. 329 ff.), and it was absolutely without decolourising power on permanganate. When wanted, a portion was diluted with about 12 volumes of water, and boiled down to half the bulk, when it was rapidly cooled. In the meantime the mineral, in quantity from 0·3 to 0·5 grm., having been introduced into the tube, about 2 c.m.[3] of distilled water was added, and brought to boiling for a few moments in order to expel air from the powder. When somewhat cooled, from 15 to 30 c.m.[3] of the dilute sulphuric acid, according to the amount of mineral and the size of the tube, was added, and then the carbonic acid, which had been allowed to generate and escape from the apparatus for some time, was introduced, and the seal was made as above described. No breakage of a tube in the oven ever occurred as a consequence of fusing the one tube into the other. The titrations were made in about half a litre of water, to which sulphuric acid had been added, as rapidly as possible, using a dilute solution of potassium permanganate, giving about 0·00036 grm. oxygen to the cubic centimetre that had been standardised by iron wire of known contents in iron and checked by pure oxalic acid, and taking account of the expansion or contraction of the titre liquid if its temperature varied more than a few degrees from that possessed by it at the time of standardisation.

Zimmerman (*Ann. d. Chem.*, 1886, ccxxxii., 285) decomposed U_3O_8 for the purpose of estimating UO_2 by concentrated sulphuric acid in a current of carbonic acid, but this method is not very applicable to uraninite, owing chiefly to its greater insolubility, particularly when rich in UO_2. Whereas, according to Zimmerman, quantities of U_3O_8 up to 1·2 grms. are decomposed thus in an hour, uraninite may be only moderately attacked after many hours boiling. The whitish green insoluble salt which soon separates out undoubtedly exerts a retarding effect in protecting the rest of the uraninite powder from the action of the acid. A couple of tests were made by this method which accorded fairly well with the others, but owing to the great uncertainty of securing complete decomposition they were not multiplied.

In the early part of the present investigation, when want of concordance in the results of UO_2 titrations was the rule, decomposition by hydrofluoric acid was sometimes employed as a method leading to the estimation of UO_2 gravimetrically, and the results go to show that this may be developed into a method of considerable accuracy, useful at any rate as a check upon the volumetric determination.

All uraninites, without exception, are decomposed completely by hydrofluoric acid, even in the cold, if time enough is given, the uranous uranium being thrown down with the earth metals and lead as an insoluble fluoride. The refractory Glastonbury variety was thus decomposed in about ten days. In order to accelerate action, the acid and very fine powder were placed in a wide and perfectly flat platinum dish provided with a loose fitting

cover, which was set in a dentist's vulcaniser containing a solution of sodium carbonate to absorb acid vapours. Dish and vulcaniser having been filled with carbonic acid gas, the lid was adjusted and a lamp placed beneath, so that decomposition should take place under high temperature and pressure, and in absence of air. The main difficulty in the subsequent manipulation, and probably the only element involving possible serious error, is the difficulty of washing the precipitate on the filter, owing to its strong tendency to run through as soon as washing begins. Experience seemed to show that this is best obviated by using water containing ammonium chloride and hydrofluoric acid, but the experiments made were too few in number to show whether the method can be developed into an exact quantitative one. An attempt will perhaps be made to perfect it. The following are some of the results obtained :—

A specimen of Glastonbury uraninite, giving on a basis of 57·43 per cent UO_2 by titration 26·48 per cent of UO_3, gave gravimetrically 26·89 and 28·58 per cent UO_3.

Another specimen from Glastonbury, giving by titration 59·31 per cent UO_2, gave gravimetrically 60·05 per cent.

Colorado unaninite, giving 58·51 UO_2 by titration, gave 58·24 per cent gravimetrically.

A few trials with U_3O_8 gave results in part less satisfactory, namely, 34·89, 31·26, and 28·47 per cent UO_2 instead of 32·07.

Assuming the practical insolubility of UF_4 in hydrofluoric acid, the method should give a tolerably exact separation of UO_2 from FeO and UO_3, and thus in connection with the oxygen used in titration indicate the state of oxidation of iron, as well as uranium, in substances containing both where one does not predominate so enormously over the other as in uraninite. Even from Fe_2O_3 the separation should be exact, unless in the moment of breaking up of the molecule the ferric iron should exert an oxidising effect on the uranous uranium before the latter is withdrawn from its influence by combination with fluorine. Hydrogen sulphide being without reducing effect on UO_3, the presence of sulphides would be immaterial so far as the separation of UO_2 from UO_3 and the oxides of iron is concerned, but of course the correct estimation of total oxygen by titration would be impossible if iron were present in its peroxidised state, or if even in its absence the hydrogen sulphide formed could not be expelled before titration.

It may be worth while before leaving the subject of estimation of uranium to add that, in accordance with Zimmerman's observations, I have met with no evidence of the existence of an oxide U_2O_5 as a result of strong heating in air; and the oxide U_3O_8, as he has so conclusively shown, is also, by my own experience, only to be obtained with its theoretical percentage of oxygen by igniting and cooling in oxygen.

(To be continued.)

Detection of the Contamination of Water with Sewage.—Peter Griess (*Ber. Deutsch. Chem. Gesell.*).— The author dilutes paradiazobenzol sulphuric acid with 100 parts of water, and adds a little soda-lye in excess. The solution must always be used when fresh, as it soon becomes coloured spontaneously. The water to be examined is placed in a tall cylinder of colourless glass holding about 100 c.c., which is placed before a window upon a white surface. To the water are then added 2 to 4 drops of the diazo-solution. The whole is well stirred up and it is carefully observed. If no change of colour takes place within five minutes we may infer the almost entire absence of organic excretions or products of decomposition. A yellow colour more or less decided shows the presence of a more or less considerable quantity of such matter. By means of this reaction the author has detected normal human urine when diluted with 5000 parts of water, and the urine of horses when diluted with 50,000 parts.

THE MANCHESTER SHIP CANAL FROM A SANITARY POINT OF VIEW.

PUBLIC attention is being authoritatively called to a serious peril to which this project—otherwise highly commendable—is exposing the towns on its banks and the districts which it intersects. Everyone knows that the population of South Lancashire is inferior in numbers to that of London alone ; that the quantity of industrial refuse to be got rid of is much larger, and that the volume of water carried by the Irwell and its affluents is very much smaller than that of the Thames. Hence it is justly contended that if all this pollution is allowed to collect in the new canal, and there to remain without regular removal by a powerful current, a nuisance will be created which it is simply fearful to contemplate. The directors of the Canal Company and their advisers, though without the gift of prophesy, might have been expected to foresee and provide against such a peril. All Lancashire men know what the river Irwell and the Bridgewater Canal have been for more than half a century. Pour the two together and the consequence must be a Stygian pool such as the world has not yet witnessed. It therefore behoves the Canal Company to be wise in time. They are being warned that unless this prospective danger is guarded against, Parliament may put its veto upon the completion of an undertaking which already presents an aspect so menacing. Surely the shareholders will consider that even the extra outlay which will be required for the sanitation of the undertaking will be a less blow to their interests than its total arrest. It will be necessary to purify the sewage and other waste waters of Manchester and Salford before allowing them to enter the canal.

This can be effected only by precipitation. The large quantity of chemicals present will be a total bar to irrigation. The foul water cannot, fortunately, be carried out to sea by any modification of the Bazalgette system. Nor can the country afford to take any more steps in the costly and wasteful way of precipitating the sewage (imperfectly) and conveying the deposit out to sea. As the *Liverpool Journal of Commerce* appropriately remarks—" Any system of sewage disposal which entails the waste of the offensive matter is essentially wrong and opposed to all principles of science and common sense."

It adds further that " no system of sewage disposal can fulfil the essential conditions unless adequate chemical precipitation is provided for, and at the same time means are adopted for the disposal of the precipitated matter as manure."

These are the very principles which we have long maintained, and we are glad to find that they are being adopted by the general press. Of course, we in London have little room to take up our parable against Lancashire as regards the neglect or rather the toleration of nuisances. The London County Council seems, unfortunately, to have inherited the errors of its predecessor, the Metropolitan Board of Works. Perhaps, indeed, such questions as Public Health are overlooked by Boards because they do not fall in with the demands of faction.

Adulteration of Rape-Oil with Fish-Oil.—O. Schweissinger (*Pharm. Central Halle*).—The following characteristics may serve for the detection of the latter oil :—

	Rape-Oil.	Fish-Oil.
Specific gravity at 15°	0·915	0·931
Saponification number	181	218
Iodine number	98	142
Melting-point of fatty acids	21	26
Congealing-point of fatty acids ..	16	19

PROCEEDINGS OF SOCIETIES.

ROYAL INSTITUTION OF GREAT BRITAIN.
General Monthly Meeting, Monday, November 2, 1891.

Sir James Crichton Browne, M.D., LL.D., F.R.S.,
Treasurer and Vice-President, in the Chair.

The following were elected Members of the Royal Institution :— George Frederick Deacon, M.Inst.C.E.; Miss Henriette Hertz; Arthur Walter Mills; Robert Mond, B.A., F.R.S.E.; Joseph Shaw; D. Hack Tuke, M.D., F.R.C.P; Lieut.-Col. H. S. S. Watkin, C.B., R.A.; and William Henry White, C.B., F.R.S., M.Inst.C.E.

The Presents received since the last Meeting were laid on the table, and the thanks of the Members returned for the same.

UNIVERSITY OF SYDNEY.

A meeting of the Senate of the University was held on Monday, September 21, 1891, at the University Chambers, Phillip Street.

A letter was received from Mr. F. B. Guthrie, resigning his office of Demonstrator in Chemistry, from January 1 next, in consequence of his appointment as Analyst to the Department of Agriculture. His resignation was accepted with regret.

It was resolved that Professor Thorpe and Professor Ramsay, of University College, London, be requested to select and appoint a Demonstrator of Chemistry to take office on March 1 next, the salary to be at the rate of £350 per annum, and £60 to be allowed for passage money, such sum to be refunded if the demonstrator should resign his office before the expiration of two years from his appointment.

FRANKLIN INSTITUTE.
(Chemical Section).
Tuesday, September 15, 1891.

Dr. W. H. Wahl, President, in the Chair.

A Paper by Mr. Cabell Whitehead, of the Mint Bureau, in Washington, on "*The Use of Cadmium in Assaying Gold Bullion*," was read by the Secretary in the absence of the author. Dr. Tuttle commented upon the paper, and discussed the most important advantages of the proposed method.

Mr. Waldron Shapleigh, of the Welsbach Incandescent Gas Light Company, of Gloucester, N.J., exhibited the following specimens of *Salts of the Rare Earths* :—

Praseodymium, neodymium, and lanthanum oxides, sulphates, nitrates, chlorides, carbonates, oxalates, acetates, and double salts with the alkaline metals.

Cerium oxide, oxalate, chloride, nitrate, and the double nitrate of the cerous and ceric oxides with ammonium.

Yttrium and erbium nitrates, oxides, and oxalates.

Zirconium oxide, nitrate, sulphate, and some double salts.

Yttrium and erbium (not separated) oxides and nitrates obtained from gadolinite, cerite, monasite, furgusonite, and samarskite. Thorium and vanadium salts.

Also large specimens of the following minerals from which these salts were obtained :—Samarskite, zircon crystals, and monazite sand from North Carolina, monazite sand from Brazil, gadolinite from Texas, and allanite from Virginia.

Mr. Shapleigh said the collection was of interest, as it is the first time the salts of praseodymium and neodymium have been shown, and probably separated in this country. Some of the salts have not been heretofore prepared.

The separation of these elements is long and tedious; the specimens shown have undergone nearly 400 fractional crystallisations, and have been in state of constant preparation since early in 1888. Tons of cerite and monazite sand have been used, and tons of the salts of cerium and lanthanum obtained, but the yield of praseodymium oxide has been only a few kilos. The percentage of neodymium is much higher.

Dr. Carl Auer von Welsbach, in 1885, was the first to separate didymium into these elements, and together with Prof. Bunsen, to determine their atomic weights; that of Pr 143·6, and of Nd 140·8. The oxides are M_2O_3, and probably M_4O_7.

With one exception, the salts of praseodymium exhibited were of a pale green, and of neodymium pink or amethystine colour.

Zirconium, lanthanum, and cerium should no longer be classed among rare earths, as hundreds of tons of ores from which they are obtained have been located in North Carolina, and there seems no end to the deposits of monazite sand—one of the richest ores, and containing most of the rare earths. In Brazil it does not have to be mined, as it is in the form of river sand. In North Carolina it is found in washing for gold.

Should the arts, trades, or manufactures create a demand for these so-called rare earths, nature could readily supply it from these two localities.

Thorium and yttrium minerals are not so easy to obtain; they have, however, recently been found in quantity in North Carolina and Texas.

Working on a commercial scale, he finds the yield of lanthanum from cerite nearly 1 per cent higher than stated in the analysis published.

NOTICES OF BOOKS.

Foundations of Chemistry. (Grundlagen der Chemie). By D. Mendeleeff, Professor at the University of St. Petersburg. Part 7. St. Petersburg: Ricker, 8vo., pp. 143.

This part of Prof. Mendeleeff's great work treats of the elements sulphur, selenium, tellurium, chromium, molybdenum, tungsten, uranium, and manganese, and begins the consideration of iron. The author considers that the interior of the earth is a mass consisting like meteorites of siliceous matter and metallic iron mixed with carbides, whilst the lighter bodies, *i.e.*, those with lower atomic and molecular weights, have collected on the surface of the globe. He points out that velocity in mechanics and velocity in chemistry have nothing in common save the idea of time.

Prof. Mendeleeff protests that Berthelot's compound S_2O_7 cannot be regarded as a persulphuric acid, since it forms no salts, and is liable to spontaneous decomposition with absorption of heat. It is properly a sulphur peroxide analogous to hydrogen, sodium, and barium peroxides.

CORRESPONDENCE.

ALLOTROPIC SILVER.

To the Editor of the Chemical News.

Sir,—In a recently published lecture, Mr. Meldola seems to call in question the existence of allotropic silver. This opinion does not appear, however, to be based on any adequate study of the subject, but to be somewhat conjectural in its nature. No experimental support of any sort is given, and the only argument offered (if such it can be called) is that this altered form of silver is analogous to that of metals whose properties have been greatly

changed by being *alloyed* with small quantities of other metals. Does, then, Mr. Meldola suppose that a silver alloy can be formed by precipitating silver in the presence of another metal from an aqueous solution, or that one can argue from alloys, which are solutions, to molecular compounds or lakes? Moreover, he has overlooked the fact that allotropic silver can be obtained in the absence of any metal with which silver is capable of combining, as in the case of its formation by the action of soda and dextrine. Silver cannot be alloyed with sodium.

Mr. Meldola cites Prange as having shown that allotropic silver obtained with the aid of ferrous citrate contains traces of iron, a fact which was published by me several years earlier, with an analytical determination of the amount of iron found. Mr. Prange repeated and confirmed this fact of the presence of iron (in this particular case), and my other observations generally, and was fully convinced of the existence of both soluble and insoluble allotropic silver. Mr. Meldola's quotation of Mr. Prange would not convey this impression to the reader.

Of the many forms of allotropic silver, two of the best marked are the blue and the yellow.

Blue allotropic silver is formed in many reactions with the aid of many wholly different reagents. To suppose that each of these many substances is capable of uniting in minute quantity with silver to produce in all cases an identical result the same product with identical colour and properties, would be an absurdity.

Gold-coloured allotropic silver in thin films is converted by the slightest pressure to normal silver. A glass rod drawn over it with a gentle pressure leaves a grey line behind it of ordinary silver. If the film is then plunged into solution of potassium ferricyanide it becomes red or blue, whilst the lines traced show by their different reaction that they consist of ordinary silver. Heat, electricity, and contact with strong acids produce a similar change to ordinary grey silver.

These reactions afford the clearest proof that the silver is in an allotropic form. To account for them on suppositions like Mr. Meldola's would involve an exceedingly forced interpretation, such as no one who carefully repeated my work could possibly entertain.—I am, &c.,

M. CAREY LEA.

Philadelphia, October 22, 1891.

THE CONSTITUTION OF BUTTER.

To the Editor of the Chemical News.

SIR,—On the 19th of January, at the invitation of the Society of Chemical Industry, I read a paper on Butter, and described an experiment on 50 grms. of butter-fat. From that experiment, which I carried out myself, and for the substantial accuracy of which I am able to vouch, I drew some important conclusions which I expect will be verified by competent observers in due course.

The experiment and the conclusions were, as I expected, distasteful to a certain section of my auditory, which was violently demonstrative in its disapproval, but, as I thought, very ineffective in its attempts at criticism. My reply, as recorded in the Society's Journal, winds up with the assertion that I had no doubt of the accuracy of the work that I had brought before the meeting.

Among my auditory was Mr. Allen, of Sheffield, who took part in the discussion, and then some months afterwards, with that fresh in his recollection, presented himself to the Chemical Section of the British Association at Cardiff, and informed the Chemical Section that Messrs. Wanklyn and Fox had never published such an experiment. Having been taken to task, Mr. Allen replies that his statement was perfectly correct as it stands, but seems to be unconscious that his statement to the Chemical Section was calculated to mislead, and no doubt did mislead, the Section.—I am, &c.,

J. ALFRED WANKLYN.

REACTIONS OF ANTIMONY AND ARSENIC.

To the Editor of the Chemical News.

SIR,—Experimenting for some time past upon the action of H_2SO_4 on the gases AsH_3 and SbH_3, I find that when either of these gases is bubbled through H_2SO_4, at 160° to 180° C., a partial decomposition of the gas takes place, with formation of a metallic mirror and a solution of the metal in the H_2SO_4 (which can be precipitated as sulphide upon cooling and adding H_2S), whilst a portion of the original gas passes over.

Obtaining a number of mirrors, "Marsh's test," I exposed them to the *hot* vapours of H_2SO_4 for (say) five minutes, and found that, whilst H_2S was without action upon them, a drop of $(NH_4)_2S$ yielded a distinct sulphide, Sb_2S_3 forming almost immediately and As_2S_3 after some time.

I next led $AsH_3 + H_2S$ through a little H_2SO_4 kept just at the boiling-point, and found that As_2S_3 was formed inside of the leading tube, just about where it dips into the H_2SO_4 and also formation of SO_2. The acid dissolves the sulphide, and it is better to continue the boiling for some time (not strong) to make sure that it is all dissolved, as a precipitate of S forms in the upper part of the tube, which might be misleading; besides, the SO_2 must be boiled off to obtain the dissolved sulphide by the addition of H_2S after cooling. $SbH_3 + H_2S$ behaves in a similar manner.

In the event of excess of AsH_3 or SbH_3 a metallic mirror will be formed. The re-precipitated sulphides, by the addition of H_2S, are fainter in colour than in an HCl solution.

This naturally suggested treating the combined gases as in "Marsh's test," and the experiment resulted in a beautiful coloured sulphide.

Here, also, excess of the metal tends towards the formation of a metallic mirror. The tube must not be strongly heated, else the newly formed sulphide is decomposed and a glazed orange-coloured residue of sulphur is left. Arsenic gives a fine yellow merging to orange and sometimes to ruby-coloured sulphide, which is nearly all deposited on the off-side of the flame. Sb gives a fine ruby-coloured sulphide having an orange edging, and is deposited upon *both* sides of the flame.

Both sulphides are soluble in NaHO, and are re-precipitated by acidifying with HCl.

I next lighted a small jet and let the flame be as *small* as possible, and pressed a cold porcelain surface on the flame. Sb yielded a pronounced orange-*red* sulphide, As a fine canary-yellow. H_2S, under the same conditions, yields a precipitate of pale yellow S, but the two are easily distinguished from one another.

As_2S_3 having the appearance of being dropped on, S has a glazed appearance. As_2S_3 is soluble in a drop of NaHO, S is not, and, when a drop of $AgNO_3$ is placed upon each, the As_2S_3 begins at once to change to brown and finally to black, whilst S is not affected. These last two reactions will be found very *definite* in colour and sensitive to the presence of As or Sb, besides having the advantage of dispensing with all intermediate reactions lying between the formations of the gas and sulphide.

With regard to details, use an ordinary $\frac{3}{4}$ test-tube for the generating of the gas, as it yields far better results than when a flask is made use of. Connect the generating tube to a three-limbed tube, do the same with H_2S flask, then to the third limb connect the tube holding the H_2SO_4, having a small leading tube reaching to the bottom of the acid. In starting let the hydrogen come away freely before passing in the H_2S, as, were it to come away first, it would pass over into the other tube and form a sulphide of the metal when its solution is put into the generating tube, and this holds good during the experiment if the H_2S be too *strong*.

When testing by the dry reaction it is better to heat at two or three points, as at the lower temperature

required more of the combined gases pass over than one flame can decompose, the presence of which can be detected by lighting a small jet of the gas. — I am, &c.,

MATTHEW FORBES.

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CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxiii., No. 16, October 19, 1891.

The Allotropic Conditions of Silver.—M. Berthelot.—The author called the attention of the Academy to the memoirs of Carey Lea on the allotropic states of silver, and exhibited specimens of the colour of gold and others of a purple colour sent him by the author. He explained the importance of these results, which remind us of the work of the ancient alchemists, but he reserved the question whether these substances are really isomeric states of silver or complex and condensed compounds, sharing the properties of the element which constituted the principal mass (97—98 per cent), conformably to the facts known in the history of the various carbons, of the derivatives of red phosphorus, and especially of the varieties of iron and steel. Between these condensed compounds and the pure elements the continuous transition of the physical and chemical properties is often effected by insensible degrees, by a mixture of definite compounds.

Calculation of the Magnetic Rotation of the Plane of Polarisation of Light.—G. Hinrichs.—A mathematical paper not susceptible of useful abstraction.

A New Process for Determining Nitric Nitrogen and Total Nitrogen.—E. Boyer.—This process is founded upon the reduction of nitric nitrogen into ammonia by oxalates and sulphur in presence of soda-lime. It is deduced from the two following experiments: If we heat to redness in a combustion tube a mixture in known proportions of neutral calcium oxalate, of sodium nitrate, and of soda-lime (0·5 grm. sodium nitrate, 5 grms. of calcium oxalate, and 15 grms. soda-lime), about two-thirds of the nitric nitrogen are reduced to the state of ammonia. This number is a maximum, and it does not vary appreciably if we increase the proportions of soda-lime and calcium oxalate to a given weight of nitrate. But if we cause simultaneously calcium oxalate and sulphur to act upon sodium nitrate in presence of soda-lime (0·5 sodium nitrate, 5 grms. neutral calcium oxalate, 15 grms. soda-lime, 2 grms. sulphur), the reduction of the nitric nitrogen to ammonia is complete. This second reaction the author has applied at first to the determination of nitric nitrogen in potassium and sodium nitrates, then to the determination of the total nitrogen in all its three states (organic, ammoniacal, and nitric) operating as follows: He first prepares a powdered mixture consisting of sulphur 1 part, calcium oxalate 2 parts, soda-lime 6 parts. In the preservation of this mixture no precautions are required save those used for soda-lime. For the analysis he weighs out 0·5 grm. potassium or sodium nitrate dried and powdered, which are intimately incorporated with 50 grms. of the mixture above described. Then into a combustion tube, 0·55 metre in length and 0·017 metre in diameter, he introduces successively, beginning with the closed end, 2 grms. calcium oxalate, for the production of the inert gas required to sweep out the apparatus at the end of the operation, 10 grms. soda-lime in powder, 10 grms. of the mixture, the nitrate to be analysed, mixed as aforesaid, 10 more grms. of the mixture, 10 grms. soda-lime in powder and finally a plug of asbestos. The

analysis is conducted exactly in the same manner as the determination of nitrogen with soda-lime. The combustion is completed in 40 minutes. The gaseous ammonia is collected in a Will-Varrentrap's tube containing an excess of sulphuric acid of known strength. The determination of the neutralised acid is effected in the ordinary manner, care having been taken to expel by ebullition any sulphuretted hydrogen and carbonic acid which may have been formed during the combustion. The quantity of a nitrate taken for analysis to 50 grms. of the mixture should not exceed 0·5 grm. sodium or potassium nitrate. 1 grm. must be taken of any substance containing nitrogen in all its three states.

The Action of Nitric Acid upon Dimethylated Ortho-Anisidine.—P. van Romburgh.—The product is a dinitro-nitrosamine of monomethylated ortho-anisidine.

Zeitschrift für Analytische Chemie.
Vol. xxx., Part 3.

Determination of Nitrogen.—O. Foerster had continued his researches on the determination of nitric nitrogen (see *Zeitschrift*, xxviii., 422). He has executed comparative determinations of saltpetre, using for the conversion of the nitric acid into ammonia phenolsulphuric acid either alone or along with zinc powder or sodium thiosulphate. The first method did not give satisfactory results. The author obtained values which agreed well with the true quantity of saltpetre on using zinc-powder as a reducing agent according to Jodlbaur's suggestion, omitting the addition of platinum chloride, and using sulphuric acid containing 5—6 per cent of phenol, which, after the saltpetre has been dissolved, is to be mixed with an equal quantity of pure sulphuric acid. He points out, however, that the zinc-powder must be added in very small portions and with refrigeration, and that a large excess of soda-lye must be used to dissolve the precipitate of zinc hydroxide. The experiments with sodium thiosulphate gave quite satisfactory results. He uses by preference a quantity of material containing 0·5 grm. of saltpetre, saturates it with water in the solution flask, distributes the solution of the saltpetre upon the sides of the flask by shaking, and evaporates down in the water-bath. There are then added 15 c.c. of a concentrated sulphuric acid containing 6 per cent of phenol, and the saltpetre is caused to dissolve in the sulphuric acid by frequently moving the flask. As this dissolving takes up some time Foerster considers that Stutzer's agitating apparatus would be useful. The saltpetre dissolves more easily in the water when it has been diffused over the surface of the flask, as above directed by previous solution in water and subsequent desiccation. If the saltpetre is used in the form of powder its solution in the phenol sulphuric acid is more difficult, and the operation must be conducted with the aid of refrigeration. After the saltpetre is perfectly dissolved from 3—5 grms. of crystalline sodium thiosulphate are added, and the acid mixture after the completion of the reaction is diluted with pure sulphuric acid, 0·5 grm. mercury having been added. To 30 c.c. of the phenol sulphuric acid there are used 20 c.c. of the pure sulphuric acid. This dilution is necessary to effect the complete oxidation of the phenol and the other organic substances. The process is then completed according to Kjeldahl's directions. Foerster regards the addition of phosphoric anhydride to the sulphuric acid as also the treatment with permanganate after the sample is dissolved. The author gives various reasons why his process is preferable to Jodlbaur's original method with zinc-powder. The presence of chlorides occasions a small loss of nitrogen, which may be avoided if, when evaporating the solution of saltpetre, the chlorine is precipitated by the necessary quantity of silver sulphate. The silver chloride formed is not in any manner injurious. For the determination of total nitrogen in presence of much organic matter,

nitrogenous and non-nitrogenous, along with nitrates the above described, according to Foerster's experiments, may be used with satisfactory results. A larger addition of pure sulphuric acid is here to be recommended, about twice as much as in the case of pure saltpetre. In many cases it is preferable to omit the previous moistening of the sample and the subsequent drying in the solution flask. On account of the strong frothing on the addition of the phenolsulphuric acid, a solution flask is selected holding 300—400 c.c., and refrigeration is applied whilst the substance is mixed with the phenolsulphuric acid.

With reference to the statements of Scovell and the Association of Official Agricultural Chemists, who recommend the use of salicylic acid in place of phenol in the Jodlbaur process, Foerster has examined whether the determination of nitric nitrogen can be effected with salicylic acid containing sulphuric acid and sodium thiosulphate. He considers salicylic acid decidedly preferable to phenol both in the analysis of pure nitrates and in the determination of total nitrogen in mixtures of nitrates with nitrogenous organic matter. To 0·5 potash saltpetre there are used 16 c.c. of sulphuric acid containing 6 per cent of salicylic acid, 5 grms. sodium thiosulphate, and 10 c.c. pure sulphuric acid. The presence of chlorides occasions in this case, within certain limits, no loss of nitrogen, so that there is no necessity for the addition of silver sulphate. Foerster has obtained perfectly accurate results in presence of about 5 per cent sodium chloride. For further experiments on this subject we must refer to the *Chemiker Zeitung*, vols. xiv. and xv.

For the determination of nitric acid in manures T. F. Schmitt (*Chemiker Zeitung*, xiv., 1410) effects the conversion of the nitric acid into ammonia by means of nascent hydrogen. He proceeds as follows:—40 c.c. glacial acetic acid and 15 grms. of a metallic mixture of equal parts of zinc powder and iron powder are put in an Erlenmeyer flask holding about 750 c.c., 50 c.c. of the solution of nitrate representing 0·5 grm. of the substance are allowed to flow in with constant agitation. The development of hydrogen begins at once and continues for about 15 minutes; after this time 15 grms. more of the metallic mixture are added. The mass often congeals to a paste, but an addition of 30 c.c. of water causes the development of hydrogen to re-commence. In 30—40 minutes the reduction is complete; 200 c.c. of soda-lye, of sp. gr. 1·25, are added, and the ammonia is distilled off in the ordinary manner. Determinations with pure nitrates gave results which agree with the theoretical quantities. The temperature must not be allowed to rise to near 89°; the glacial acetic acid must be present in sufficient excess to combine immediately with all the ammonia; and the soda-lye added after the completion of the reduction must suffice not merely to neutralise the residual excess of acetic acid, but to keep the dissolved zinc hydroxide in solution. The author concludes from his experiments that this method may be used as a substitute for the Jodlbaur process in the determination of total nitrogen in organic matter mixed with nitrates, by first reducing and then heating with concentrated sulphuric acid. A. F. Holleman (*Chemiker Zeitung*) has not found this process quite satisfactory. F. Scheiding (*Chemiker Zeitung*) writes concerning the Schulze-Tiemann method of determining nitric nitrogen. He also proposes an apparatus for collecting and measuring nitrogen when the method of Dumas is used.

Comparison of the Congealing-Points of Different Tallows.—Finkener.—This paper requires the accompanying figure.

Volumetric Determination of the Acidity of Oils.—Holde.—In case of pale oils in the ethereal solution, of which the colour reaction of phenolphthalein may still be observed, 10 c.c. of the sample are measured out, the measuring vessel is rinsed out with a mixture of 8 parts ether and 2 parts absolute alcohol containing phenolphthalein and neutralised, and the liquid after the

addition of the rinsings is titrated with alcoholic soda, 1 c.c. of which is equivalent to 0·005 grm. SO_3, until a permanent red colour appears. In case of dark oils 20 c.c. of oil and 50 c.c. of absolute alcohol are well shaken up in a cylinder. After the two strata have become separated 25 c.c. of the alcoholic stratum are mixed with alcohol and ether containing phenolphthalein and titrated as above.

Sophistication of Bergamot Oil.—Schimmel and Co. point out that the specific gravity of the genuine oil must not be below 0·880; its optical rotation not more than +20° (for a column of liquid of 100 m.m.). The oil must form a clear solution in ½ part of alcohol at 90 per cent by volume, and the solution must not become turbid on the addition of alcohol of the same strength. The residue should form a green homogeneous mass.

Detection of Ground Wood in Paper.—W. Herzberg.—The well known detection of ground wood-stuff by the red colouration obtained with phloroglucine and hydrochloric acid is not always decisive, as metanyl yellow, which is much used in paper making, is coloured red by acids. There is, however, a difference in the appearance of the colour. If phloroglucine is placed upon paper containing ground wood there is very gradually formed a red colour which increases in depth, whilst the thicker fibres are conspicuous by their darker colour. The spot fades away gradually without being surrounded by a halo. In presence of metanyl yellow the spot appears at once in its entire depth of colour; it fades in a few minutes and is surrounded by a violet halo. In case of the presence of hemp, unbleached jute, fibres of Adansonia, &c., certainty cannot be attained with a microscopic examination.

Examination of Opium and its Alkaloids.—A note by Euger Dieterich (*Pharm. Central Halle*), and P. C. Plugge (*Archiv. der Pharmacie*).

Determination of Urea.—Papers by Mörner and Sjögvist (*Skand. Archiv. fur Physiologie*), E. H. Bartley (*Journal of the American Chemical Society*), and C. J. H. Warden (CHEMICAL NEWS).

Detection and Determination of Hydrochloric Acid in the Gastric Juice.—Notices by Salkowski and Kumagawa (*Archiv. fur Pathologie Anat.*), Sansoni and Molinari (*Annali de Chimica*), Moritz (*Archiv. fur Klin. Medicine*), Favizky (*Archiv. fur Pathologie Anat.*), Bourget (*Archiv. de Med. Exper.*), F. A. Hoffmann (*Central Blatt. fur Klin. Medicine*), and A. Jolles (*Monats'hefte fur Chemie*).

Atomic Weight of Bismuth.—R. Schneider (*Journ. Prakt. Chemie*).—The author objects to the results of A. Classen, and considers the value 208 more probable than that given by Classen. Classen (*Journ. Prakt. Chemie*) replies that Schneider's contention is not based upon experimental evidence.

Atomic Weight of Magnesium.—W. M. Burton and L. D. Vorce.—(From the CHEMICAL NEWS).

The Equivalent Weight of Fluorine. — Henri Moissan.—(From the *Comptes Rendus*).

Journal of Inorganic Chemistry. — A journal embracing the entire field of inorganic chemistry is about to be issued by Leopold Voss, 18, Hohe Bleichen, Hamburg. The editor will be Prof. Dr. Gerhard Krüss, of Munich (Herzog Heinrich-strasse 4). The new paper will be devoted to inorganic researches and to theoretical treatises belonging to this sphere. Analytical methods of a purely scientific character are admissible, but those which relate to technical chemistry are excluded. It will be admitted that for a quarter of a century inorganic chemistry has ceased to be a merely descriptive discipline, and has begun to participate in the decision of theoretical questions. A number of the most eminent cultivators of inorganic chemistry will co-operate in the new undertaking.

NOTES AND QUERIES.

$*_*$* Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Laboratory without Gas.—In reply to "F.I.C.'s" query, I beg to inform him that I have worked a tolerably large laboratory for nine years in a gas-less district with the following appliances. For heating, boiling, distilling, &c., I use a Rippingille's "Hero" stove, which burns petroleum. If the top of this stone be covered with wire gauze it will be found a most satisfactory substitute for the ordinary Bunsen. For larger distillations, &c., at higher temperatures, I use a "Duplex Hero," which is also convenient for heating a small drying oven or water-bath. The "Giant Hero" will heat a large drying oven or a number of heaters, &c. I can recommend these stoves highly for simplicity, efficiency, and non-liability to get out of order. For low heats I use either the common or the Argand spirit-lamp, and the Russian blast spirit-lamp for small fusions. For very high temperatures Fletcher's gasoline blowpipe answers every purpose and is also adaptable to this maker's excellent portable furnaces for metallurgical work. With such an outfit "F.I.C." should never feel the want of gas. I shall be glad to supply any further information as to details which he may require.—BRYAN CHARLES WALLER, M.D., F.I.C.

Laboratory without Gas.—In answer to the query of "F.I.C." I desire to say that I was chemist at a large iron works in England in the laboratory of which there was no gas. The principal heating arrangement in use was a large sand-bath heated by means of a coal fire. It was not unlike a baker's oven, only more open, and in place of the stone floor there was a layer of 3 or 4 inches of fine sand, the heat being regulated by a damper. Being always accustomed to the use of gas heaters I took very badly to this arrangement at first, but after getting into the way of using it I greatly preferred its use to that of gas Bunsens or Argands. In a properly built furnace the heat can be regulated by the damper to a nicety, and the furnace is so arranged in relation to the sand-bed that the heat gradually increases from the front (or outside edge) to the back. A constant supply of distilled water can also be had by making use of the heat from this fire.—D. J. P.

TO CORRESPONDENTS.

H. E. H.—Persoz evidently means by "A B" Baumé's araeometer. There is no certainty which of the existing scales of that instrument he used. It can scarcely have been the American.

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DETERMINATION OF THALLIUM.

By M. H. BAUBIGNY.

IN the earlier researches made upon thallium the sparing solubility of thallous iodide in water suggested this compound as a means of determining this metal. In fact, experiment has proved that the iodide is almost the only salt utilisable for this purpose. It is less soluble than the bromide and the chloride, and stable even above 100°, whilst the peroxide and the sulphide—the most insoluble compounds—are affected by desiccation. Still the insolubility of the iodide in water is not sufficient for the degree of accuracy required in analysis. It is only when the liquid contains certain salts, and especially potassium iodide, as observed by Lamy, Willm, and Werther, that the solubility of thallous iodide is considerably less and becomes null.

Willm, who has practised this method of determining thallium, says that it is far from being exact, since a fraction of the iodide always dissolved towards the end of the washing. On the other hand, Werther, whilst pointing out certain erroneous facts, has not freed the question from uncertainties and difficulties which still remain entire.

A study of the question has convinced me that by observing certain rules the gravimetric determination of thallium may be effected with the greatest accuracy. Thus :—

1. Willm's complaint that the method is deficient in accuracy must be imputed solely to his method of procedure. Towards the end he washed the precipitate with distilled water, and of course dissolved some thallous iodide.

2. We must reject as erroneous Werther's assertion that this iodide is insoluble in ammoniacal water; for if it is certain that the acidity of the liquid promotes solubility, and that it is better to operate in a neutral or an ammoniacal liquid, it is no less certain that the mere presence of ammonia is insufficient to obviate the solubility of the iodide in water, and that we no more ought to complete the washing with ammoniacal water than with pure water. Further, the solubility is even increased, as it may be proved by comparative determination if to the ammoniacal solution we add a little clean ammoniacal salt, sulphate or chloride.

3. The solubility in weak alcohol is not so great as Werther alleges ; for if at 13°, in alcohol at 85°, the coefficient of solubility, given by Werther $\frac{1}{50800}$, were correct, we should have 11 m.grms. metallic thallium per litre, and at this concentration alkaline sulphides would immediately give a precipitate of sulphide. But if we shake up thallous iodide, pure and recently precipitated with alcohol marking 78° at the temperature of 22° (1 vol. of water and 3 vols. of alcohol at 98°), and allow it to digest for twenty-four hours, and then reduce the filtrate to one-fifth of its value by slow evaporation, the aqueous liquor which remains is not even coloured by ammonium sulphide.

If to these data we add that thallous iodide is insoluble in a solution of potassium iodide at 1 per cent, and that potassium iodide is still moderately soluble in alcohol at 82° (4 vols. of alcohol at 98° and 1 vol. of water), we have all the conditions necessary for the total separation of thallium contained in a saline solution.

As for the precipitation, Willm recommends to effect it in the cold and to wait for twelve hours before filtering. Werther operates in heat and filters a few hours afterwards. Experience shows me that it is preferable to operate in heat at 80° to 90°. The precipitate collects better, and the adhesion to the glass of which Willm complains is almost null. The only precaution to be taken is to filter after cooling, when the liquid is quite clear, which is accelerated by setting the beaker in cold water. The orange precipitate, very fine at first, is transformed into a yellow powder, heavy and crystalline, which passes less readily through the filters.

From these observations there results a simple and rational procedure. The thallium is precipitated in heat by an excess of potassium iodide in a neutral solution, so that the liquid after precipitation may still contain 1 per cent of the potassium iodide, which is easily effected by operating with a solution of iodide of known strength. It is filtered by decantation, and repeatedly washed with a solution of potassium iodide at 1 per cent, in order to remove foreign salts, and the washing is completed with alcohol at 80° to 82°.

The precipitate is decanted upon the filter and dried. The collected filtrates and washings, when reduced to a small volume, never showed thallium sulphide when tested with an alkaline sulphide. It is of course necessary to ascertain previously that all the metal is in the thallous state, otherwise it must be reduced to that state by a little sulphurous acid.

When the product is dried there is a further difficulty. The volatility of the thallium compounds and of the metal itself, if heated rather strongly in presence of a reducing body, *e. g.*, a filter, interferes with the incineration of the filter if we wish to avoid all loss. Hitherto a filter tared after desiccation at 100° has always been used. We know the imperfections of this method and the many uncertainties which it involves. I have therefore sought a way of escape, and have found a very simple procedure. The bulk of the thallous iodide is removed from the filter, and upon the small quantity which remains attached to the filter there are let fall a few drops of hot dilute nitric acid (2 vols. of water to 1 vol. of acid at 36°). The iodide is decomposed; it is washed in a little hot water, and all the thallium is carried away as nitrate. The liquid, collected in a small tared porcelain capsule, is gently evaporated to dryness with a few drops of HCl. The chloride formed is decomposed by a drop of a concentrated solution of potassium iodide, which converts the thallous chloride into iodide mixed with iodine from the reduction of a little thallic salt, formed in presence of nitric acid. But thallous iodide, as I have found by direct experiment, is decidedly fixed, even at 170°, —at least its weight does not vary appreciably, even after heating for several hours. The small excess of iodine is therefore expelled by heating for some hours to 170°. The thallous iodide which has been previously collected is poured into the crucible, and the whole is weighed.—*Comptes Rendus* (cxiii., Oct. 26, 1891).

EXPERIMENTS RELATING TO IMPROVEMENTS IN THE MANUFACTURE OF METALLIC SODIUM.

By H. N. WARREN, Research Analyst.

IN the general process for the manufacture of metallic sodium, one of the greatest drawbacks at the present time is the difficulty of expelling the sodium as quickly as reduced in the form of vapour, insomuch that, for a considerable time after, a most intense heat has been obtained : on viewing the inside of the converters large globules of melted sodium are not unfrequently observed, which are only with difficulty volatilised. Potassium, on the other hand, although presenting more difficulties than sodium as regards its preparation, melts and volatilises at a much lower temperature; for instance, if 23 parts by weight of sodium be carefully alloyed with 29 parts of

potassium, a fluid amalgam is produced which remains liquid at all ordinary temperatures; if this amalgam is now distilled in a non-oxidising atmosphere, in the first place potassium metal distils over, leaving a residue consisting of sodium containing about 5 or 6 per cent of potassium : this alloy, which resembles ordinary sodium in appearance, is much more energetic than that substance itself, taking fire when thrown upon the surface of water the same as potassium, but burning with the characteristic yellow flame of the former.

Following up these reactions several mixtures were obtained for reduction, by calcining sodium tartrate in admixture with a sufficiency of potassium tartrate to allow of about 5 or 6 per cent of potassium to pass into the distillate; the reaction being brought about in wrought-iron tubes, and urged to whiteness by the aid of a small blast furnace.

The globules of metal thus obtained presented in appearance an exact similitude with the first-mentioned alloy, and were considerably more volatile than pure sodium. The iron tubes after cooling were cut longitudinally, and in no instance could any reduced metal be detected; the metals as fast as reduced having been volatilised, producing the aforesaid alloy.

The calcining of tartrates on a large scale would naturally be entirely out of place; but the introduction of potassium could, as far can be seen, be brought into play when employing any of the ordinary commercial methods, save that the percentage of the two would probably have to be looked into still closer in order to obtain concordant results.

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DETERMINATION OF SMALL QUANTITIES OF ALKALI AND RECOGNITION OF THE NEUTRALITY OF WATER.

By F. MYLIUS and F. FOERSTER.

(Continued from p. 229).

FOR the preparation of mille-normal solutions we must use pure or, at least, neutralised water, since otherwise the alkaline impurities derived from the glass vessels in which the water is preserved have a decidedly disturbing effect. Mille-normal solutions can be kept for some time in bottles of good glass. The titration is advantageously conducted in a small stoppered bottle, from 50 to 100 c.c. of the aqueous liquid under examination being shaken up with 10 to 20 c.c. of an ethereal solution of iodeosine containing 2 m.grms. of the colouring matter per litre. Such a solution, which appears almost colourless, can be obtained by diluting the ethereal solution of iodeosine to be mentioned below. If free alkali is present, the lower stratum, after shaking, appears rose-coloured, whilst on neutralisation with alkali it becomes colourless again. The titration is best completed by again adding so much solution of alkali that a distinct rose colour reappears. The small excess of about 2 c.c. thus produced must be deducted from the total quantity of solution of alkali consumed.

The influence of carbonic acid upon titration with mille-normal solutions, according to the process above described, is not important. Even on titration with decinormal solutions, using an ethereal solution of iodeosine, it interferes little, as is shown by the following experiment :—For neutralising 40·7 c.c. decinormal sulphuric acid, which, when tested with litmus (the carbonic acid having been previously expelled by heat), required 40·7 c.c. of a decinormal solution of sodium carbonate, there were consumed, when an ethereal solution of iodeosine was used as indicator, 41·2 c.c. of the soda solution in order to pro-

duce a distinct red colouration. Decinormal soda-lye consumed equal quantities of decinormal hydrochloric acid, whether litmus or an ethereal solution of eosine was used as an indicator. In its behaviour with carbonic acid, there is consequently a decided contrast between iodeosine and phenolphthalein, although the two differ but little in their chemical nature.

The following instances may show the varied applicability of the method :—

The carbonates dissolved in spring- or well-water may be quickly and easily determined. The acid consumed is equivalent to the " combined " carbonic acid in the water. 5 c.c. water from the Charlottenburg mains consumed for neutralisation 15·2 c.c. N/1000 sulphuric acid, which corresponds to 6·7 grms. of " combined " carbonic acid in 100,000 water. Titrations of drinking-water have been effected with centinormal solutions, using carmine as indicator.

The solubility of calcium carbonate in pure water which has been repeatedly determined can be readily shown by this method. Finely pulverised marble was well washed, and then left for some time in contact with neutral (see below) water which had been previously deprived of carbonic acid by ebullition in platinum vessels. 25 c.c. of the solution thus obtained, after the lapse of seven days, required for neutralisation 15·5 c.c. N/1000 sulphuric acid. A litre consequently contained 31 m.grms. calcium carbonate in solution. The decomposition of neutral salts of ammonium, when their solutions are heated, can be shown by means of titration with mille normal solutions. A decinormal solution of commercial crystalline ammonium sulphate in " neutral " water, which was itself neutral, was distilled in the apparatus to be described below. Appreciable quantities of ammonia were present in the distillate; 200 c.c. were three times distilled off in succession; 25 c.c. of the first distillate required for neutralisation 32·5 c.c. N/1000 sulphuric acid; the same quantity of the distillate required 34·5 c.c., and of the third 37 c.c. of the acid. Hence it appears that the concentration of the solution in the distillatory vessel increases little. The ammonia present in the 600 c.c. of water distilled was 0·01416 grm. NH_3, *i.e.*, 0·83 per cent of the total ammonia present.

The eosine reaction is particularly useful for testing the neutrality of salts.

If a salt is considered neutral the solution of which, on shaking with ethereal solution of eosine, is turned red by a minimum of mille-normal soda-lye, many of the salts sold as pure are not neutral. Thus, *e.g.*, 5 grms. of Kahlbaum's sodium chloride required for the production of a red colour 1·1 c.c. N/1000 soda-lye, corresponding to the presence of 0·0008 per cent hydrochloric acid. The same preparation, after ignition, was found to be faintly alkaline, since 5 grms. required 1·4 c.c. N/1000 sulphuric acid for neutrality. As regards the alkaline sulphates, further observations are needed. We merely remark that a commercial and apparently pure specimen of potassium sulphate had a distinctly alkaline reaction.

The recognition of the neutrality of salts of the zinc group has hitherto been especially difficult, but iodeosine was here found to be the most sensitive indicator. The hydroxides of metals of the zinc group, like the alkalies and alkaline earths, form with iodeosine soluble salts of a reddish violet. In the solutions of the basic salts a red colour appears on shaking up with ethereal solution of iodeosine; but the slightest excess of free acid prevents the appearance of salts of colouring-matters.

For the production of neutral zinc sulphate, the commercial salt, having an alkaline reaction, was twice recrystallised from a carefully neutralised solution; 5 grms. of the crystals dissolved in water and shaken with ethereal solution of eosine gave a colourless solution; but 2 c.c. N/1000 alkali sufficed to produce a distinct rose colour.

(To be continued).

THE REASON OF THE SPARING SOLUBILITY OF CHEMICALLY PURE ZINC IN ACIDS.

By JULIUS M. WEEREN.

SINCE De la Rive in 1830 made the observation that chemically pure zinc is almost insoluble in dilute sulphuric acid, this puzzling and interesting phenomenon has been the subject of research, but without meeting with a satisfactory explanation. The question derives increased importance from the fact that other metals, if pure, and other acids behave in a similar manner. Nitric acid alone attacks most metals considerably, even if chemically pure.

Since it has been found that the same metals, which in a chemically pure state were almost insoluble in acids, are always more or less rapidly attacked by the same acids when impure, the attention of investigators was turned to the impurities and the adherents of the contact theory recognised in this different behaviour of the pure and the impure metals,—a defence against the attacks of the supporters of the chemical theory.

According to the contact theory the electric current arises in a closed circuit (Zn, Pt, H_2SO_4) by the origination of a difference in the electrical potential due to the contact of the two metals. This difference tends to be equalised by the acid. But as an electrolyte—in this case the sulphuric acid—cannot conduct the electric current without itself being decomposed, such a decomposition of the acid is effected by the current which passes from the zinc through the sulphuric acid to the platinum. The hydrogen is set free upon the platinum and the acid radicle, in virtue of its liberated affinities combines, with the zinc to form zinc sulphate. In brief, the contact theory views the solution of the zinc as a consequence of the electric current running from the zinc to the platinum in consequence of the electric opposition of the two metals; the zinc must remain undissolved as long as no electric difference is present. Hence impure zinc, but not pure zinc, dissolves in acids.

The contact theory thus seemed to solve the problem in a simple and natural manner, and in consequence it met with almost universal acceptance.

But this explanation did not agree with the facts that chemically pure metals are, in general, easily dissolved by dilute sulphuric acid, if boiling, as also by cold nitric acid. These reasons led me to give up the theory above given, and to seek elsewhere for the cause of the insolubility of pure metals in acids. In this investigation I ultimately succeeded and found an explanation for the phenomena at once simple and comprehensive.

I maintain that chemically pure zinc or other chemically pure metals are insoluble or sparingly soluble in acids, because at the moment of their immersion in the acid they are at once enclosed in an atmosphere of condensed hydrogen, which under normal conditions makes any further action of the acid impossible. This immeasurably thin but everywhere continuous layer of hydrogen is alone the cause of the insolubility or sparing solubility of chemically pure zinc in dilute acids.

Absolute insolubility is from various reasons out of the question if we consider that both the varying density of the surface and minimal traces of foreign metals, such as we may suppose even in chemically pure zinc, must give rise to very feeble local currents, which are of course attended with a slight solution of the zinc.

It is known that on the action of nitric acid upon the zinc there are formed, according to the concentration of the acid, NH_3, N_2O, NO, N_2O_3, and N_2O_4. There is at first formed upon the zinc hydrogen, which in its nascent tate is at once oxidised to water by the excess of nitric acid, whilst the latter is reduced to the above mentioned nitrogen compounds. Where then are the latter formed? Certainly not directly on the surface of the zinc, from which they are separated by that stratum of water which

has been formed by the oxidation of the nascent hydrogen. This stratum is certainly very thin, but it suffices to abolish the attraction between the metal and the gas which is formed. Zinc, therefore, on treatment with nitric acid, is never enclosed in a protective coating of gas, but it is exposed on its entire surface without protection to the attacks of the nitric acid.

The conditions of impure zinc if treated with sulphuric acid are similar. The hydrogen formed is not liberated on the zinc, but on the accompanying impurities which are more negative than zinc. Consequently the true surface of the zinc remains always free from gas, so that the action between metal and acid goes on continuously.

Similar results are obtained also with cadmium, cobalt, nickel, iron, and aluminium. Aluminium, which is otherwise scarcely or not at all attacked by dilute sulphuric or nitric acid, dissolves easily in these acids in a vacuum. It dissolves also readily in a vacuum in a perfectly neutral solution of ferric chloride which is reduced to ferrous chloride with an escape of hydrogen. At the ordinary atmospheric pressure this process is much more tedious.

It would be interesting to ascertain whether hydrogen gas alone possesses the property of condensing in its nascent state upon metals, and of thus rendering them unattackable by acids, or if this property is common to other gases. If this is not the case we are entitled to assume that in these phenomena of adhesion the metallic character of hydrogen plays a part of greater or less importance, and that we have here a transition to the compound of palladium and hydrogen.—*Ber. Deut. Chem. Gesell.*, vol. xxiv., p. 1785.

ELECTROLYTIC DETERMINATION OF METALS AS AMALGAMS.[*]

By G. VORTMANN.

(Continued from p. 228.)

Determination of Zinc.

IN 1885 C. Luckow recommended the separation of zinc as amalgam from a weak sulphuric solution. I can confirm the accuracy of his statement, but a large excess of free acid may completely prevent the separation. I therefore preferred to undertake the precipitation of the zinc from the solution of the double ammonium oxalate or from an ammoniacal solution.

1. *Separation of Zinc from the Solution of the Double Oxalate.*—The zinc salt along with a weighed quantity of mercuric chloride was dissolved in water in a platinum capsule and mixed with an excess of ammonium oxalate (3—5 grms.). On electrolysis the zinc amalgam was deposited upon the platinum capsule as a silvery white layer and could be washed without loss. To ascertain whether the precipitation was complete a portion of the liquid was tested with ammonium sulphide. The mercury must not be in too large a proportion to the zinc (to one part zinc not more on the outside than 2—3 parts mercury), as the zinc is otherwise deposited in a spongy form. Moreover zinc is easily deposited without mercury, the addition of which has merely the purpose to facilitate the removal of the deposit from the platinum capsule. Like the other amalgams zinc amalgam does not require to be transferred rapidly to the balance, as it neither loses nor gains weight if left in the exsiccator for a considerable time.

2. *Separation of Zinc from an Ammoniacal Solution.*—The precipitation of zinc as an amalgam from an ammoniacal solution containing tartaric acid takes place similarly to that from the double oxalate; a larger quantity of mercuric chloride must, however, be used (to 1 part zinc at least 3 parts of mercury), as the amalgam otherwise falls off in scales. A large excess of mercury is in this case not hurtful.

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[*] *Berichte Deutsch. Chem. Gesell.*

The amalgam, whether deposited from solution of ammonium oxalate or from an ammoniacal liquid, is readily dissolved by dilute nitric acid; there remains a black powder consisting of platinum black which adheres to the capsule but is easily removed by friction. If the capsule is weighed after removal of the zinc amalgam, rinsing with alcohol and ether, and desiccation, it has its original weight, or it weighs only 1—2 m.grms. more than before the electrolysis. After the removal of the black powder, the weight of which is sometimes very appreciable, the loss of weight of the capsule is sometimes only a few m.grms., but occasionally may reach 5 centigrms. On account of this loss of weight the separation of zinc as amalgam cannot be recommended, and the previous method, according to which the capsule is first coated with copper or silver, is to be preferred.

Determination of Cadmium.

Cadmium, like zinc, can be separated as an amalgam, either from the solution of the double ammonium oxalate or from an ammoniacal solution. The latter is more uniform if the mercury is present in large excess (at least 4 parts to 1 part of cadmium); if but little mercury is present the amalgam separates in a crystalline form and does not adhere sufficiently to the platinum, so that it cannot be easily washed without loss. If the amalgam contains 4—6 parts of mercury to 1 part cadmium, it is so hard that it may be rubbed with the finger without removing any portion. If the quantity of the mercury is eight times as large as that of cadmium, the amalgam is in part liquid. It does not become oxidised in the air, and can be preserved for several days without any change in its weight. Dilute nitric acid dissolves it readily, and as a rule, without a residue of platinum black; rarely is a faint blackness perceptible.

As cadmium ammonium oxalate is less soluble in water than the corresponding zinc salt, and as a larger quantity of mercuric chloride must be dissolved, the oxalate method is suitable only for the separation of small quantities of cadmium (about 0·2—0·3 grm.).

The solution containing the salt of cadmium and the mercuric chloride is mixed with about 5 grms. ammonium oxalate, stirred up, and diluted as far as possible with water. The ammonium oxalate must be dissolved in the cold, as on the application of heat a precipitate of mercurous chloride may be produced in a concentrated solution.

If the quantity of cadmium exceeds 0·3 grm. an ammoniacal solution must be used. In this case the solution of the cadmium and the mercuric salt is mixed with about 3 grms. tartaric acid and then with ammonia until it smells strongly, diluted with water, and exposed to the electric current until a portion of the liquid is not rendered turbid by an addition of ammonium sulphide.

Determination of Lead.

1. *Separation of Lead from Acid Solutions.*—In the determination of lead as an amalgam, I encountered difficulties, as the lead was partly separated out at the positive electrode as a peroxide, and cannot be removed readily by reducing agents, or, in some cases, not at all. Tartaric and oxalic acids, ethylic alcohol, potassium iodide had little effect. The removal of the lead peroxide was best effected by means of nitrous acid. I dissolved the lead salt and the mercuric chloride in water; adding 3— 5 grms. sodium acetate and a few c.c. of a concentrated solution of potassium nitrite. The white precipitate formed was dissolved in acetic acid. The clear yellow solution thus obtained was submitted to electrolysis. As long as the liquid contained nitrous acid, no lead peroxide was formed, but towards the end of the process there appeared on the positive electrode a brown stain, which quickly disappeared on the addition of a few drops of solution of potassium nitrite. When a portion of the liquid gave no colouration with ammonium sulphide, the liquid was decanted off, the lead amalgam was

rapidly rinsed with water, alcohol, and ether, quickly dried by warming the capsule in the hand whilst a current of air is directed upon it, and then placed in the exsiccator.

The lead amalgam, when dry, is permanent in the air, and does not vary in weight if it remains for twenty-four hours in the exsiccator. In a moist state, it is readily oxidised; hence, after rinsing with water, that liquid must be removed as quickly as possible with alcohol and ether. Oxidation, however, is not so rapid as to render the determinations inaccurate; the moist amalgam undergoes no change for about five minutes. It then gradually loses its lustre, and is coated with a yellowish white film. It is readily soluble in nitric acid, and leaves on the platinum capsule a very faint stain of platinum black.

The separation of lead as amalgam can also be effected in an aqueous solution acidulated with dilute nitric acid, to which a little potassium nitrite is added in order to prevent the formation of lead peroxide. As the quantity of nitrite which a liquid containing free nitric acid can take up without a violent escape of nitrous acid is very trifling, there is formed at the positive electrode during electrolysis a thicker layer of lead peroxide than in an acetic solution. It must be re-dissolved by the frequent addition of a few drops of the solution of potassium nitrite. The analysis is in this case more tedious than with an acetic solution, and must be continued until no more lead peroxide is deposited at the positive electrode, and until no lead can be detected in the liquid by means of ammonium sulphide.

The determination of lead as amalgam has the advantaee of being applicable to larger quantities of the metal than the process at present in use.

(To be continued).

DETERMINATION OF MANGANESE IN MANGANIFEROUS SLAGS AND ORES.

By G. L. NORRIS, Pencoyd, Pa.

THE manganese in slags from blast furnaces making spiegel, and in open hearth slags, is easily and rapidly determined in the following way:—

One grm. of the finely powdered slag is placed in a 4-ounce Griffin beaker, moistened slightly with water to prevent caking, and 50 c.c. of nitric acid of 1·42 sp. gr. added. Bring to a boil, and while the slag is in suspension add 3 or 4 c.c. of hydrofluoric acid. The slag is rapidly decomposed and the silica driven off. Boil the solution for a few minutes to drive off any remaining hydrofluoric acid, then transfer to a larger beaker or a precipitating flask, add more nitric acid, bring the solution to a boil, and precipitate the manganese with potassium chlorate. Filter off the manganese dioxide upon an asbestos filter. The manganese dioxide may either be dissolved in standardised oxalic acid or ferrous sulphate solution, and the excess of the solvent titrated with permanganate of potassium, and the amount of manganese calculated; or the manganese may be finally weighed as the pyrophosphate.

For manganese in ores:—1 grm. or 0·5 grm., according to richness of the ore, is placed in a 4-ounce Griffin beaker, moistened with water, and 50 c.c. nitric acid of 1·42 sp. gr. added. Bring to a boil and add a few small pieces of tartaric acid. Ores made up largely of the mixed oxides of manganese go into solution readily. When the solution clears, add a little hydrofluoric acid to decompose the residue. Where there is much oxide of iron in the ores it is better to add the hydrofluoric acid along with the tartaric acid.

Drive off any remaining hydrofluoric acid, and be sure that the tartaric acid is all decomposed. Add more nitric acid, boil, and precipitate the manganese with potassium chlorate.

The nitric acid breaks up all the other oxides of manganese into the oxide and dioxide, and dissolves the monoxide, while the tartaric acid causes the solution of the dioxide. Considerable tartaric acid may be used, as it is readily decomposed by boiling in the nitric acid solution.

By this method the manganese can be determined in about forty-five minutes, while a much longer time is required by the ordinary way of solution in hydrochloric acid, with separation and fusion of the residue and consequent accumulation of salts.—*Journal of Analytical and Applied Chemistry*, August, 1891.

A METHOD OF OBTAINING AMMONIA-FREE WATER.

By D. B. BISBEE.

A VERY easy way of obtaining ammonia-free water, which I have used for some time and have never seen mentioned, is to acidulate the water, before distilling, with sulphuric acid. The acid holds all ammonia in the retort, the first portions even of the distillate being ammonia-free. But this acidulation naturally causes the nitric and nitrous acids in the water to distil over. For some purposes, however, nitrates are not objectionable. At the laboratory of the Iowa Agricultural Experiment Station, Ames, Iowa, when we wish to obtain chemically pure water for any use, we take distilled water, which is nitrate-free, acidulate with sulphuric acid, and distil, at once getting *pure* water.—*Journal of Analytical and Applied Chemistry*, August, 1891.

THE USE OF CADMIUM IN ASSAYING GOLD BULLION.*

By CABELL WHITEHEAD,
Assayer to the Mint Bureau.

CADMIUM, as a substitute for silver in assaying gold bullion, was first used by Balling (Crookes's " Select Methods in Chemical Analysis "). He states that the gold is entirely parted from all metals, except the platinum group, when its alloy with cadmium is boiled with strong nitric acid for one hour, followed by a second boiling for ten minutes with fresh portion of same acid. For general assays of gold bullion I do not think that Balling's method with cadmium will bear comparison in point of accuracy with the old one of quartation with silver and cupellation. But, with certain modifications which will be suggested later, it will be found rapid and satisfactory for a preliminary assay.

It is, however, in the estimation of small quantities of silver in gold bullion containing considerable amounts of copper or platinum, that I have found cadmium to be a most efficient aid.

The difficulty in determining silver in the presence of platinum by cupellation is well known to assayers. In such cases the following has been the method in the United States Mint at Philadelphia:—

An approximate assay is made by cupellation, after which, and based on this approximation, enough pure silver is added to 500 m.grms. of the bullion to make in all at least 1004 m.grms. of silver present in the assay. This weighed silver and bullion is wrapped in a sheet of lead weighing 2·5 grms., and the whole placed on a hot cupel in the muffle furnace.

As soon as the lead "clears" the cupel is withdrawn; when cold the button is flattened and put in a bottle such

as is used in the humid assay of silver, dilute nitric acid is added and heat applied. When action ceases, the silver present in solution is determined volumetrically as usual. The silver found, less the amount added, gives the silver in 500 m.grms. of bullion.

There are two objections to this method: (1) The insolubility of lead nitrate in nitric acid necessitates the use of dilute acid, which leaves much alloy with the gold; (2) the alloy to be removed is one-third silver. This is very important when small quantities of silver are to be determined, as in the case of gold coin, which rarely contains more than 0·003. Cornets, after three boilings with acid (ten minutes each), retain from 0·001 to 0·002 of silver; so it will be seen at a glance that the amount retained after one boiling with dilute acid will be much greater, and the gold residue will contain more silver than was present in the original bullion.

The presence of 10 per cent or more of copper in high grade gold bullion makes the accurate determination of silver by cupellation impossible. Not only is gold taken into the cupel in large quantities by the copper, but it is also left in specks over the entire surface covered by the assay, thus making a " proof" practically worthless.

The method which I am about to describe was devised for the estimation of silver in gold coin, and has been in use in the laboratory of the Bureau of the Mint for the past year, where it has given such satisfactory results that it is thought a brief description may prove of interest to others engaged in the same line of work.

Five hundred m.grms. are weighed into a porcelain crucible and covered with 10 grms. of potassium cyanide. The potassium cyanide is melted over a Bunsen burner or preferably a blast lamp. When the cyanide is in quiet fusion 1 grm. of cadmium is dropped into the crucible, where it quickly melts and forms a bright, homogeneous alloy with the gold. After gently shaking, so as to bring the cadmium in contact with every particle of bullion, the crucible is removed and the contents poured on a clean porcelain slab, where it soon solidifies. The alloy will be found in one piece and is easily detached from the potassium cyanide. It is now washed in warm water, dried, and placed in a diamond mortar, when several sharp blows with a hammer quickly reduce it to powder.

This powder is carefully transferred to an assay bottle, 1004 m.grms. of pure silver added and 10 c.c. of nitric acid—32° Baumé—poured on. In from five to ten minutes (depending upon the heat used) the solution is complete and all action has ceased. The bottle is now cooled and 100 c.c. of normal salt solution is charged and the bottle shaken. The precipitation is finished with the decinormal solution.

This assay is accompanied by another called a "proof," made of 1004 m.grms. of pure silver dissolved in the same amount of acid. Now the excess of silver found in the assay, over that shown in the "proof," is the amount contained in 500 m.grms. of coin. This doubled gives parts of silver per thousand.

Example :—An alloy composed of 499 m.grms. pure gold, 1 m.grm. of silver, and 1 grm. of cadmium, treated as above described, after being charged with 100 c.c. normal salt solution, required 5 c.c. decinormal solution for complete precipitation of the silver present. A proof assay, carried along as check, upon 1004 m.grms. of pure silver, required in addition to 100 c.c. of normal salt solution, 4 c.c. of decinormal solution for complete precipitation = to 1004 c.c. decinormal solution. Hence, each c.c. decinormal equals 1 m.grm. silver, and 1 c.c. decinormal solution required by the bullion, in excess of that called for by the silver added, shows the bullion to contain 1 m.grm. silver in 500, or 2 parts per 1000.

It may be asked by those not familiar with mint appliances and usages, " Why not titrate directly the silver brought into solution with the cadmium instead of adding a known weight of pure silver and finding the desired result by difference ?"

The reply is that the small amount of silver present in this class of bullion would, as chloride, not " clear " on shaking, and much time would be consumed in finding the end reaction. By the method described the usual apparatus and solutions may be availed of and results rapidly obtained.

When no such reasons exist the sulpho-cyanide method alluded to at the end of this article is recommended.

Example in Gold Bullion.

An approximate assay gives by cupellation 0·035 silver, hence 500 m.grms. will contain about 17·5 m.grms. of that metal, and 986·5 m.grms. must be added to bring the total silver up to 1004 m.grms. If copper is not present about 50 m.grms. is added, it being found that the alloy of copper with cadmium is very brittle, and the resulting button is easily crushed to powder.

The sample having been fused with cadmium in presence of potassium cyanide is powdered and subjected to treatment with nitric acid as above described.

After charging with 100 c.c. normal salt solution, and shaking, the assay required 4·5 c.c. decinormal solution for end reaction. A "proof" consisting of 1004 m.grms. pure silver in solution, treated in same manner, required but 3 c.c. decinormal solution.

Hence the assay contained $4·5 - 3 = 1·5$ m.grms. more silver than the proof, or $1004 + 1·5 = 1005·5$ m.grms. in silver in all. This, less the 986·5 m.grms. silver purposely added, gives 19 m.grms., as the silver present in 500 m.grms. of bullion taken, or thirty-eight parts in each thousand instead of thirty-five parts found by cupellation.

In favour of the new method it may be said—

(1) That the ready solubility of cadmium in nitric acid of any strength makes it possible to dilute (if the term may be used), the silver present in gold bullion, to any desired extent, while, on the other hand, the difficult solubility of lead necessarily limits the dilution possible by the time required for its even imperfect extraction.

The inevitable small portion of other metals retained by the gold after treatment with nitric acid may therefore, by the use of cadmium, be made to contain but an infinitesimal quantity of silver.

(2) The brittleness of the button obtained permits its being crushed to a powder, in which condition the alloy rapidly yields its soluble portion to nitric acid, and the time required for an assay is materially shortened.

(3) The low temperature required enables the chemist to dispense with all special appliances. A Bunsen burner will well answer the requirements for heating purposes, and little more is needed beyond a standard salt solution. No muffle or rolls are wanted.

In a laboratory where few assays are made the following method might be followed and very satisfactory results obtained. After alloying and crushing, treat in a parting flask with 15 c.c. of nitric acid, 32° Baumé, for ten minutes; pour off this acid into a beaker, add 15 c.c. acid same strength and boil for ten minutes longer, pour off again in same beaker, wash with hot water and take out in an annealing cup, dry and heat over blast lamp, weigh and deduct 0·25 m.grm. for cadmium retained. Twice this weight gives the gold fineness.

The acid and washings are evaporated to drive off free nitric acid, and silver determined either as chloride, or volumetrically with sulphocyanide with ferric indicator. Cadmium nitrate does not interfere in the least with determination of silver, either as chloride or as sulphocyanide.

Detection of Paraphenetidine in Phenacetine.— L. Reuter.—The author introduces 0·5 grm. of the specimen into 2·5 grms. of melted chloral hydrate and mixes. If the phenacetine is pure the solution is clear and colourless. But mere traces of paraphenetidine colour the solution at once of a more or less intense violet.— *Zeitsch. f. Anal. Chem.*, xxx., Part 3.

ON THE OCCURRENCE OF NITROGEN IN URANINITE, AND ON THE COMPOSITION OF URANINITE IN GENERAL.*

By W. F. HILLEBRAND.

(Continued from p. 233.)

Detection and Examination of Nitrogen.

AT an early stage in the work it was noticed in a few instances, where the sealed tubes in which UO_2 was to be estimated were left in an upright position for a short time, that an extremely slow disengagement of gas took place, which was especially noticeable if the tubes were gently tapped on the table occasionally, whereby the bubbles enmeshed by the powder were set free and rose through the liquid in the tube. This was supposed to be due to the presence of traces of carbonates in the mineral, and no particular attention was paid to it, although it seemed strange that they should not be entirely decomposed in a very few moments after contact with the acid. Later, when making the first estimation of UO_2 in Glastonbury uraninite above mentioned with hydrofluoric acid, solution in this case being made in the cold and with free access of air, it was observed that this slow escape of gas was continuous throughout the whole ten days required for decomposing the mineral. This seemed to exclude the possibility of its being carbonic acid, and it was determined to collect and examine it if possible. This was done in a manner to be hereafter described.

It may be here mentioned that U_3O_8 and UO_2 prepared from the residues obtained during this work, when examined under conditions precisely similar to those obtaining with uraninite, failed to give off the least trace of gas.

The gas was colourless, odourless, a non-supporter of combustion, unchanged by mixture with air, neutral to moistened litmus papers, not absorbed by caustic alkalies, and insoluble in water; at least its coefficient of absorption was so small as to be inappreciable without elaborate experimentation.

In a Bunsen's absorption tube, containing gas from the original bröggerite, a potash ball caused no diminution in volume, neither did potassium pyrogallate, thus showing the absence of carbonic acid and of oxygen. Transferred from the absorption tube to a eudiometer, the gas was then subjected to the tests prescribed by Bunsen (" Gasometrische Methoden," 2nd ed., pp. 73, 74.

	Units.
Reduced initial volume	14·01
After exploding with oxyhydrogen.. ..	13·21
After a second similar treatment	13·20
After addition of hydrogen (32·79).. ..	45·99
After explosion with oxyhydrogen	45·93
After addition of air in excess..	181·82
After exploding	132·81
Contraction..	49·01

Two-thirds of which, or 32·67, is almost exactly the volume of the hydrogen introduced. Were it not for the relatively large contraction after the first explosion, 0·80 units, representing 5·71 per cent of the initial volume, the above tests would indicate almost incontestably that the gas could be nothing but nitrogen. Considering the small volume operated upon, and the great disadvantages under which the eudiometric experiments were made, the above is not a surprising error, and, since in other experiments it did not recur, I have no hesitation in regarding it as without significance.

Gas liberated from bröggerite by hydrochloric acid had, after treatment in the absorption tube, in the eudiometer,—

	Units.
A reduced initial volume of	27·73
After addition of hydrogen (25·77).. ..	53·50
After exploding with oxyhydrogen	53·17
After addition of air	178·08
After exploding	138·20
Contraction	39·88

Two-thirds of which, or 26·58, is sufficiently close to the volume of hydrogen added to show the purity of the gas.

Gas evolved from Branchville uraninite by sulphuric acid gave in the eudiometer—

	Units.
An initial volume of	17·98
After exploding with oxyhydrogen.. ..	18·11
After addition of hydrogen (20·37).. ..	38·48
After exploding with oxyhydrogen	37·36
After addition of air	106·32
After exploding	77·74
Contraction	28·58

Two-thirds of which, or 19·05, is nearly that of the hydrogen introduced. The admission of a trace of air into the eudiometer with the gas, or later with the hydrogen, would account for the slight contraction after the second explosion, and for the deficiency in the observed over the calculated final contraction. But such an assumption is hardly necessary, for the final readings on the eudiometer tube were very uncertain.

The evidence as to the nature of the gas, while fairly conclusive, was thus far purely negative. Proof of a more positive character was needed, and this was sought in various ways.

Long-continued passage of the electric spark between the platinum wires of the eudiometer, in which was a mixture of the gas with pure oxygen, produced a marked contraction, and a few drops of water purposely introduced above the mercury before turning on the current gave—when taken out and tested with diphenylamine, and brucine—intense blue and red colours, respectively. Blue litmus paper was turned red by it. When the terminals of a Ruhmkorff coil were connected with a simple modification of Siemens's induction tube, devised for the employment of small quantities of gas, containing a mixture of the gas with 3 volumes of electrolytic hydrogen, a slow but constant contraction resulted, provided that the product of combination as fast as formed could be removed by water or an acid. A strip of moistened red litmus paper suspended in the apparatus turned deep blue, and water used as an absorbent gave a strong alkaline reaction with litmus, besides affording with Nessler's reagent the characteristic ammonia reaction in a marked manner. With a dilute hydrochloric acid as an absorbent there was obtained 0·0190 grm. of ammonium-platinic chloride, which when heated with sodium hydrate gave off a strong ammoniacal odour, and a strip of red litmus paper held above the mixture was instantly turned deep blue. The nitrogen calculated from the above weight of $(NH_4)_2PtCl_6$ is 0·00121 grm., or nearly 1 c.c. at 0° C. and 760 m.m. The roughly measured contraction of the mixed hydrogen and nitrogen gases was in accordance with this determination. It should be hardly necessary to say that all these chemical tests were duplicated simultaneously in blank.

In a Geissler tube, under a pressure of 10 m.m. and less, the gas afforded the fluted spectrum of pure nitrogen as brilliantly and as completely as was done by a purchased nitrogen tube. In order that no possibility of error might exist, the tube was then reopened and repeatedly filled with hydrogen, and evacuated until only the hydrogen lines were visible. When now filled with the gas and again evacuated the nitrogen spectrum appeared as brilliantly as before with the three bright hydrogen lines added.

The success of these electrical experiments with Geissler and Siemens tubes is very largely due to Dr.

William Hallock, of the physical laboratory of the Geological Survey, for whose ever ready assistance and ingenuity in meeting difficulties I cannot too strongly express my appreciation.

Estimation of Nitrogen.

The original apparatus for collecting the gas is depicted in the accompanying figure.

The decomposing vessel, A, is simply a fractional distillation flask of not more than 100 c.m.³ bulb capacity, drawn out at the top to allow of connection by means of rubber tubing with the receiver B, which should approach the cylindrical in form, be provided with two closely-fitting wide-bore stopcocks, and have a capacity of 25 to 30 c.m.³. The very fine powder having been introduced into A and boiled with a few cubic centimetres of water to expel air, connection is made with B by tubing firmly wired, the receiver is suitably supported by a clamp so that A shall have the position given in the as yet empty water-bath, and the flasks c, d, e are placed in position, fitted with corks and tubes as represented, but not yet closed by the corks. A rubber tube being now attached
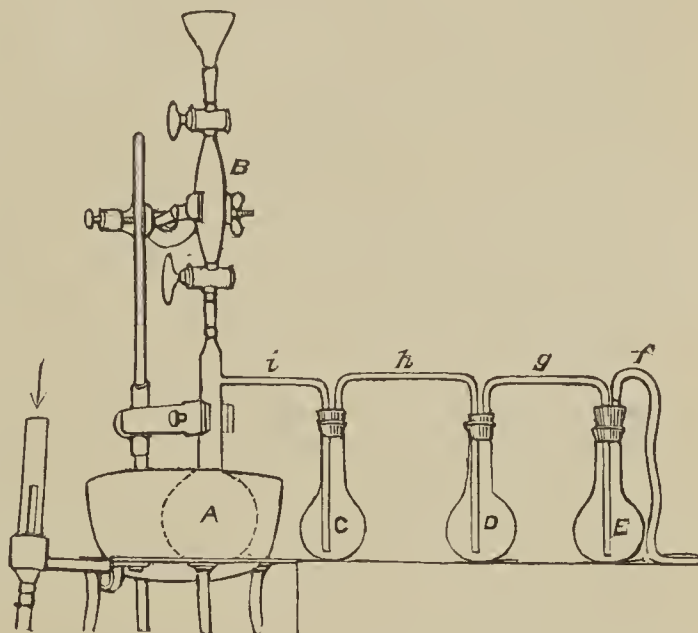
to B at the top, a thoroughly boiled sulphuric acid having the strength of that used for UO_2 estimations—

$$(1H_2SO_4 : 6H_2O \text{ by volume})$$
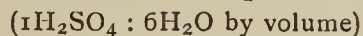
is poured into c, and continuously sucked into A and then into B until the latter is full above the upper stopcock, when this is instantly closed. c is then filled up with the same acid, and the water-bath with water to relieve somewhat the strain on the rubber connection between A and B. e and d are now filled with freshly boiled distilled water, and the cork of e is pressed down. Then by blowing in at f the air in g is expelled, and d can be corked without retaining the least bubble of air. By continuing the blowing h may be freed from air and c tightly corked. A may now be clamped in position for greater security, and a tin cover provided with a slit for the neck of A placed over the water-bath. This is primarily to prevent the action of steam on the rubber connection between A and B, by which after several days it is softened and injured, and secondarily to economise heat. On top of B is attached a small short-stemmed funnel, which is kept filled with distilled water, in order to insure a water seal about the stopcock and certain exclusion of all air. Heat is now applied to the water-bath, which is provided with a constant level arrangement and flow of water, so that it may be heated night and day without interruption. Soon an evolution of gas begins, the bubbles rise through A and the lower stopcock into B, and continue until the

mineral is entirely decomposed. The fine powder which is carried up into B by the bubbles may be in great measure returned to A by tapping B, and if not it is decomposed by the moderately warm acid in B, especially in case a readily soluble uraninite is being treated. The tube *i* should be very nearly horizontal, in order to prevent any of the powder reaching c as it falls from B. What little may collect along *i* itself will decompose in time, and the gas from it reach B. The outlet tube of E not being closed, free movement and escape is afforded for water in E as acid in B is displaced by gas. c, D, and E likewise act as checks to the diffusion of air into B. One or at most two flasks would suffice where readily soluble uraninites are treated, and the duration of the experiment is at most twelve hours, but for refractory varieties a third is indispensable. The greatest difference exists between North American and Norwegian uraninites as to their solubility in sulphuric, hydrochloric, hydrofluoric, and even nitric, acids. Whereas the Colorado and both Connecticut uraninites are not entirely decomposed by nine days' continuous treatment at 100° C. with dilute sulphuric acid in the above-described apparatus, and even the much altered North Carolina mineral requires five days for solution, all the Norwegian specimens examined are completely attacked in much less than twelve hours, and one (from Arendal) in three. Hydrochloric acid was used in one instance in place of sulphuric in the apparatus and with about the same effect.

When no gas is any longer given off the mineral is decomposed, as may be seen by removing the water from the bath and examining the residue in the bottom of the flask. It is either pure white sulphate of lead, or dark coloured if columbite was mixed with the uraninite. Owing to the large volume of acid used there is no separation of insoluble uranium or thorium salts as in the UO_2 estimations.

When the operation is ended B is disconnected from A after closing the lower stopcock, and the gas can then be readily transferred to a graduated and rather narrow measuring tube, or it can be measured in the receiver itself, if this is graduated, by opening the lower stopcock under water and allowing the latter gradually to displace the acid in order that the vapour tension of pure water may prevail. All necessary thermometric and barometric readings having been made, the volume in cubic centimetres is reduced to 0° C. and 760 m.m., and multiplied by the weight of 1 c.c. (0·001256 grm.) of nitrogen, in order to obtain the weight whence the percentage is obtainable.

The error due to absorption of a portion of the gas by the acid liquid, or by the water with which it is displaced in measuring, is a vanishing quantity, because of the high temperature of the acid at the time of disconnecting and the low coefficient of absorption of both liquids for the gas. If transferred from the receiver to a measuring cylinder the gas comes into contact with so much water that the element of absorption might have slight effect were time enough allowed; but the water levels within and without the measuring vessel having been brought into approximate accord, the temperature of the gas is reduced in a very few moments to that of the water by allowing a running stream of the latter to impinge on the top of the vessel and flow down on all sides, a thermometer being fastened thereto by a rubber band.

If necessary to use the solution for the titration of UO_2, disconnection of the apparatus and transfer of the gas can be so carried out that the result of titration is very nearly as exact as by the method already described.

The above described apparatus is well enough adapted for the estimation of nitrogen in readily decomposable uraninites, and admits of constant observation of its rate of evolution; but if the heating is continued beyond a few days, the glass of that portion of the decomposing flask under water becomes devitrified and more or less cracked. This does not necessarily prevent several days' further heating, but the danger of breakage is consider-

able. Moreover, but one experiment can be conducted at a time unless several sets of apparatus are available. Therefore recourse was had, in many cases, to decomposition in sealed tubes, exactly as described for UO_2 determinations, larger quantities up to 1 grm. of mineral being used, however, and the heating prolonged, if necessary, for two or three days, to secure complete decomposition. After opening the tubes under water, the gas was at once transferred by displacement of water to a test-tube not too large to be closed by the thumb, a piece of potassium hydrate was rapidly inserted, the thumb placed over the mouth of the tube, and the latter agitated under water to dissolve the alkali and secure absorption of the carbonic acid. This was effected in a few moments, when pure water was allowed to displace the potash solution, and the gas was then transferred to the graduated tube and measured as before.

While the two methods of obtaining the nitrogen by decomposing with an acid gave pretty satisfactory results, it was desirable to estimate it by an entirely different process if possible. Fusion with alkaline hydrates produced no perceptible evolution of ammonia, and a quantitative combustion of bröggerite, mixed with sugar by the soda-lime method and absorption of any ammonia by hydrochloric acid, furnished an amount of $(N_4)_2PtCl_6$, representing but 0·03 per cent of nitrogen. Fusion with alkaline carbonates, however, liberated nitrogen gas, and furnished a means of estimation that compared well with the acid method. The process was conducted as follows :—

The substance mixed with sodium-potassium carbonate, in a porcelain boat inclosed in a cylinder of platinum-foil open at both ends, was introduced into the rear end of a combustion tube already containing a considerable layer of copper oxide in the centre, followed by 8 inches of copper gauze plugs toward the front end. To the rear was attached a tube filled with manganese carbonate, and to the front a nitrometer containing potassium hydrate solution.

Repeated heating and cooling of the copper oxide and copper in a continuous current of carbonic acid having reduced the gas unabsorbable by the alkali solution to the smallest possible limit, heat was applied under the boat. The evolution of gas began long before incipient redness, and had to be soon checked by regulation of the temperature. Finally the heat was raised to fusion, and maintained there till the absorption of gas bubbles by the alkali was as complete as before beginning the experiment. The gas was then measured and reduced to 0° C. and 760 m.m., with due regard to the vapour tension of the alkali solution, Kreussler's (*Zeit. f. Anal. Chem.,* 1885, xxiv., 445) table being used in this connection.

Of course the small quantity of nitrogen from which it is impossible to free the carbonic acid, even in a blank experiment, and which cannot be allowed for with accuracy because it may vary slightly in each experiment, produced an uncertainty in the readings of the nitrometer, but one of very slight importance, since an admixture of even ½ a c.c. of such nitrogen could affect the result by about 0·06 per cent at the most when 1 grm. of mineral had been used. The platinum cylinder is a very necessary shield to prevent spattering of the contents of the boat on to the glass tube.

By this fusion in carbonic acid the lead contained in uraninite is apparently entirely reduced to the metallic state, and collects in globules. This reduction is probably caused by the UO_2 of the mineral, notwithstanding the fact that litharge is not reduced when thoroughly mixed with U_3O_8 or UO_2 and fused with sodium-potassium carbonate, under the conditions of the above experiment and for the same length of time. In the one case 2 molecules already existing must be torn asunder in order to admit of a re-arrangement of their constituent atoms, while in the other these constituents are assumed to exist already united in a single molecule, and in the moment

of its breaking up are most favourably situated for re-arrangement.

Nitrogen obtained in this way from Glastonbury uraninite was submitted in the eudiometer to the same ordeal as that obtained by acid, with the following results :—

	Units.
Reduced initial volume	84·69
After exploding with oxyhydrogen	84·95
After addition of hydrogen (29·02).. ..	113·97
After addition of oxygen (25·12)	139·09
After exploding	94·40
Contraction	44·69

Two-thirds of which, or 29·79, is nearly the volume of hydrogen added. The gas then is the same as that disengaged by acids.

(*To be continued.*)

PROPERTIES OF PRECIPITATES, &c.*

By E. WALLER, Ph.D.

(Continued from p. 230).

H_2TiO_3 or Titanic Acid.

Rem.—Two forms, one tolerably easily soluble in acids, the other insoluble, except in very strong acids or by fusion, are known to exist. The "insoluble" form is obtained by boiling the solution acid with sulphuric. The small amounts of phosphoric acid present in iron ores and other minerals interfere somewhat with the complete separation on boiling.

Cond.—Dilute solution containing but little free H_2SO_4. HCl and chlorides should be absent. Long boiling is necessary, the bulk of the solution being maintained. Fe, if present, should be in the ferrous form. $HC_2H_3O_2$ favours the precipitation. The best conditions for the separation of titanic acid are boiling an acetic acid solution reduced by SO_2.

Sol.—The soluble form is attacked by the same solvents as $Fe_2(OH)_6$. The "insoluble" form is slowly soluble in hot concentrated HCl or H_2SO_4, or by fusion with $KHSO_4$.

Contam.—Fe_2O_3, Al_2O_3, SiO_2, and P_2O_5. Some iron inevitably is converted to Fe_2O_3, and separates with the precipitate. By re-solution, reducing, and re-precipitation, almost all can be removed. Al_2O_3 is prevented from con-taminating the precipitate by the larger proportion of free acid. SiO_2 may be expelled after ignition by treating with HFl (or NH_4Fl) and H_2SO_4. P_2O_5 by fusion for some little time, with Na_2CO_3, and washing with dilute Na_2CO_3 solution, which leaves behind Na_2TiO_3, soluble in acids.

Ign.—Converted to TiO_2. Retains some SO_3; removable by adding a few pieces of solid ammonium carbonate and re-igniting. Volatilised by ignition with HFl, alone or with an insufficient amount of H_2SO_4.

$(xNa_2O,TiO_2)Na_2TiO_3$. Sodium Titanate.

Rem.—Usually obtained by fusing material containing TiO_2 and P_2O_5 for some time, to convert them into sodium salts, and then to separate them by lixiviation. Chiefly of service as a step in the determination of phosphorus in titaniferous ores.

Cond.—Long fusion at a fairly high temperature is necessary. A repetition of the fusion of the portion in-soluble in water, with a fresh lot of sodium carbonate, is at least necessary in order to prove the efficiency of the first fusion.

Sol.—Dissolved by acids; to some extent by water alone. Insoluble in solution of Na_2CO_3. The washing (leaching) of the insoluble portion should be continued until the washings begin to run cloudy.

Contam.—As usually applied to iron ores or precipitates from solutions thereof, the insoluble residue may contain besides sodium titanate, Fe_2O_3, acid sodium silicates, alkaline earth carbonates, &c.

$2ZnCO_3.3Zn(OH)_2$. Basic Zinc Carbonate.

Rem.—Usual precipitant, Na_2CO_3. Flocculent at first, becoming more granular by boiling.

Cond.—Solution should not contain caustic or bicar-bonated alkalies or any ammonia salts. If CO_2 is evolved by addition of the reagent, it must be boiled out. Only fixed alkalies besides the zinc should be present.

Sol.—Dissolved by dilute acids, fixed caustic alkalies, bicarbonates, and ammonia salts; also by organic solu-tions. A very large excess of fixed alkaline chlorides hinders or partially prevents the precipitation. Insoluble in water and small amounts of fixed alkaline carbonates.

Contam. — Alkaline carbonate, necessitating several washings by decantation with boiling water to remove it. Fe_2O_3,—Al_2O_3,—SiO_2. By dissolving the precipitate in HCl after ignition, Al_2O_3 and SiO_2 are left insoluble; on precipitating the solution with ammonia, re-dissolving and re-precipitating two or three times, $Fe_2(OH)_6$ is separated. These impurities may then be ignited, weighed, and deducted.

Ign.—Converted to ZnO, which in itself is not volatile. In contact with C or reducing substances, metallic zinc which is volatile may be formed.

$ZnNH_4PO_4$.

Rem.—Usual precipitant, $NaNH_4NPO_4$. Some prefer Na_2HPO in presence of ammonium salts, The best method of procedure is to add the alkaline phosphate to the acid solution and then to neutralise the hot solution by adding ammonia, little by little, finally to heat, im-mersing the beaker in a boiling water bath until free NH_3 is expelled and the precipitate is crystalline. The solu-tion containing the precipitate cannot be boiled without bumping vigorously. The precipitate can be dried at 100° and weighed as $ZnNH_4PO_4$, or ignited and weighed as $Zn_2P_2O_7$.

Cond.—Oxalates should be absent. Large excess of ammonium chloride or acetate should be particularly avoided. Practically, the solution should only contain alkalies besides the zinc.

Sol.—Dissolved by acids, excess of ammonia, ammo-nium oxalate, chloride, or acetate,—especially if hot. The solvent effect of the chloride and some other ammonium salts is to a very great extent diminished by the use of an excess of alkaline phosphate (about three times as much as is required to afford the compound).

Ign.—If heated up too rapidly some loss may be ex-perienced. In contact with C, a partial reduction to metal and consequent loss may occur. The precipitate should be carefully separated from the filter-paper and the same burned separately, or it may be dissolved by means of dilute nitric acid into a weighed capsule and the solution evaporated and finally ignited.

After ignition the precipitate is usually opaque, white, somewhat sintered together; sometimes, without apparent reason, it fuses to a glass.

$ZnS.H_2O$.

Rem.—Usual precipitant, H_2S in neutral solution, or one acid with some organic acid (acetic, citric, formic, &c.). Precipitation can be effected (though slowly) in H_2SO_4 solution; the smaller the proportion of free H_2SO_4 the more complete the separation. NH_4Cl favours its separation in a granular form, and checks a tendency to run through the filter-paper, which it sometimes exhibits, especially when the solution contains free ammonia. Oxidises slowly on exposure to the air.

Cond.—Solution should be alkaline or acid only with some of the weaker organic acids. Free mineral acids prevent the precipitation to a greater or less extent.

H_2SO_4 has the least effect, HCl the greatest. Boiling facilitates the formation of the precipitate, but increases the solvent power of acids upon it. Fe should be absent.

Sol.—Dissolved by dilute HCl and HNO_3 or by moderately strong H_2SO_4 when not. Insoluble in alkalies, neutral solutions, and in organic acids, though the latter when in excess retard somewhat its formation. Free ammonia has a similar effect.

Contam.—MnS or Ni,CO and Fe sulphides. Fe should be separated previously. From the others it may be freed by re-solution, neutralising, and re-precipitating.

$2MnCO_3.H_2O$.
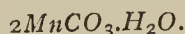
Rem.—Na_2CO_3 usual precipitant. When precipitated cold, white and flocculent—by boiling becomes granular and assumes a light brownish shade, probably from oxidation.

Cond.—Solution should not contain bicarbonates or ammonia salts. If CO_2 is evolved by the addition of the precipitant to an acid solution, it must be boiled out. Solution must be rendered alkaline by the reagent.

Sol.—Dissolved by dilute acids, bicarbonates, ammonia salts, and solutions containing citrates, tartrates, sugar, &c. Also by solutions containing large amounts of fixed alkaline salts.

Contam.—Alkaline carbonate requiring several washings (by decantation) with boiling water to remove it. Fe_2O_3,—removed by repeated solution in HCl and re-precipitation with ammonia after igniting the precipitate. SiO_2 by dissolving the ignited precipitate in acid and filtering off.

Ign.—In contact with air gives black Mn_3O_4 non-volatile. Recent investigations tend to show that the composition is not absolutely constant. If alkali has not been washed out, ignition in contact with the air affords alkaline manganate.

$MnNH_4PO_4$.

Rem.—Usual precipitant, $NaNH_4HPO_4$ or Na_2HPO_4 in presence of ammonium salts. Best managed by adding the reagent to the *acid* solution of Mn, boiling, and then adding ammonia little by little to the boiling solution, until a slight excess is present, then heating on the water-bath until the precipitate assumes *completely* the crystalline form.

Cond.—The Mn must be entirely in manganous form, and solution alkaline, though not strongly so. An excess of phosphate (about three times as much as is required to form the combination) must be present. Oxalates must be absent, as well as excessive amounts of ammonia salts or free ammonia.

Sol.—Dissolved by acids. Somewhat soluble in decided excess of ammonia, in NH_4Cl, and some other ammonium salts. The solubility in these last is neutralised by the presence of an excess of the precipitant. When too large proportion of ammonia is present, the precipitate, which should be white or faintly pinkish, becomes deeper in colour, sometimes quite brown.

Contam.—Practically none if bases forming insoluble phosphates are absent and moderate care is used in washing.

Ign.—Converted to $Mn_2P_2O_7$. The temperature should not be too rapidly raised or there may be some loss. The peculiar nacreous lustre of the precipitate is more pronounced after ignition. Sinters somewhat. Not volatile.

(To be continued).

Royal Institution. — The Christmas Lectures to Juveniles will this year be on "Life in Motion; or, the Animal Machine" (experimentally illustrated), and will be delivered by Professor John G. McKendrick, M.D., F.R.S., Professor of Physiology in the University of Glasgow.

ELIZABETH THOMPSON SCIENCE FUND.

THIS fund, which has been established by Mrs. Elizabeth Thompson, of Stamford, Connecticut, "for the advancement and prosecution of scientific research in its broadest sense," now amounts to $26,000. As accumulated income will be available December next, the trustees desire to receive applications for appropriations in aid of scientific work. This endowment is not for the benefit of any one department of science, but it is the intention of the trustees to give the preference to those investigations *which cannot otherwise be provided for*, which have for their object the advancement of human knowledge or the benefit of mankind in general, rather than to researches directed towards the solution of questions of merely local importance.

Applications for assistance from this fund, in order to receive consideration, *must be accompanied by full information*, especially in regard to the following points : —

1. Precise amount required. Applicants are reminded that one dollar ($1.00 or $1) is approximately equivalent to four English shillings, four German marks, five French francs, or five Italian lire.

2. Exact nature of the investigation proposed.

3. Conditions under which the research is to be prosecuted.

4. Manner in which the appropriation asked for is to be expended.

All applications should reach, before December 10, 1891, the secretary of the Board of Trustees, Dr. C. S. Minot, Harvard Medical School, Boston, Mass., U.S.A.

It is intended to make new grants at the end of 1891.

The trustees are disinclined, for the present, to make any grant exceeding three hundred dollars ; decided preference will be given to applications for smaller amounts.

(Signed)   HENRY P. BOWDITCH, President.
            WILLIAM MINOT, junr., Treasurer.
            EDWARD C. PICKERING.
            FRANCIS A. WALKER.
            CHARLES-SEDGWICK MINOT, Secretary.

October, 1891.

NOTICES OF BOOKS.

Arithmetical Physics. Part II., A. *Magnetism and Electricity* (Elementary and Advanced Stages). By C. W. WOODWARD, B.Sc., Principal (Chemistry and Physics Department) Municipal Technical School, Birmingham. Third Edition. Containing several New Lessons entitled "Qualitative Exercises on Lines of Force." London : Simpkin, Marshall, Hamilton, Kent, and Co. Birmingham : Cornish Bros.

COMPILATIONS of the type of the work before us seem to find no inconsiderable amount of favour. The cause of this is not far to seek. They lend themselves easily to the Anglo-Chinese system of education, *i.e.*, preparing for and passing "exams." Nor do we in the least deny that if kept in strict subordination to intelligent laboratory work they may be exceedingly useful. But we fear that in some institutions the student is trained to solve arithmetical conundrums on physical or chemical questions rather than to do real work. It is well known that for a time the introduction of the physical and natural sciences in college and school curricula met with scant sympathy among official educationalists, on the ground that such subjects did not readily lend themselves to examinational purposes. Mr. Woodward's works, and others of a similar tendency, have smoothed over a part of this difficulty.

Our author is of opinion that "some critics feel alarmed when a book has examination questions in it." Our feeling is not alarm, but regret—regret, not so much at

the publication of such questions, as at the system which gives them any value. Every " coach " has on hand collections of former examination papers, and can calculate, with a very fair degree of accuracy, what questions are likely to be put by any given examiner.

The "conscientious teacher"—if he is suffered to exist —aims at training his students to observe accurately and completely, and to draw right conclusions from the phenomena observed. We have had the pleasure of noticing elementary works which proceed on this principle.

CORRESPONDENCE.

CHEMICAL ANALYSIS AND THE PURITY OF WATER.

To the Editor of the Chemical News.

SIR,—In the *British Medical Journal* of October 24th, under the heading " Chemical Analysis and the Purity of Water," there appears an answer to a correspondent— " Medicus "—who had forwarded what purported to be an " analysis " of some water, together with an enquiry as to whether the water referred to was " likely to cause typhoid fever." The heading of this answer as well as the wording of a part of it may be wrongly interpreted.

It is stated—and quite correctly so—that " in the present state of knowledge no chemical analysis would justify the assertion that a water was likely to cause a particular disease." This statement might be taken to imply that some other form of analysis—bacteriological or microscopical, for example—might justify such an assertion; and there exists quite enough misconception about processes for the sanitary examination of water, and more especially about the capabilities of bacteriological examination, to make it highly desirable that the statement should not be understood in the sense indicated above.

As a matter of fact, no process of examination whatever which is capable of practical application for sanitary purposes, will, in the present state of knowledge, warrant the assertion that a water would produce, or would be likely to produce, a particular disease such as typhoid fever. Some over-enthusiastic bacteriologists certainly commited themselves, prematurely, to a contention very like this, and appeared to imagine that waters would be " condemned " or " passed " according to the positive or negative results of cultivation processes applied for the purpose of isolating and recognising specific pathogenic micro-organisms.

Assuming even the possibility of obtaining absolutely positive indications when operating under the necessarily restricted conditions appertaining to sanitary work; by the very nature of the processes of elimination necessary, such results could only be attained with waters which in all probability would already have been condemned by ordinary chemical and microscopical examinations of a tolerably coarse description. But, what is more important, the person who was bold enough to assert the safety of a water upon negative bacteriological results would be an enthusiast of the most dangerous character. Indeed, as was pointed out by Dr. Whitelegge and myself, in 1884 (*Transactions of the Society of Medical Officers of Health*), bacteriological processes in water analysis merely afford an additional test, of a very uncertain kind, for organic pollution. Nothing of a practical nature has been introduced since to justify any stronger assertion. It is noteworthy, by the way, that the counting of micro-organisms (which, when carefully applied, is interesting, if not very valuable) in some hands, even those of " eminent " persons, yields results which are wholly ludicrous.

These notions about the bacteriological " testing " of water have to some extent been fostered by a clumsy attempt which was made some years ago to depreciate the value, for sanitary purposes, of the chemical analysis of water—an attempt mainly based upon what one of its authors was pleased to term " experiments," but which really consisted of a series of extraordinary ceremonies performed with typhoid stools, London tap water, and Winchester quart bottles. The fallacies underlying this so-called investigation have long since been pointed out, and the statements resting upon it shattered; but the trail of the thing is to be found sometimes, and has, in my opinion, shown itself in the present case.—I am, &c.,

CHARLES E. CASSAL.

Mount Street, W., October 28, 1891.

SAPONIFICATION OF BUTTER.

To the Editor of the Chemical News.

SIR,—I am sorry to learn that Mr. Wanklyn is not satisfied with my last letter. Having myself a perfect knowledge of the circumstances, I have perhaps failed to realise that Mr. Wanklyn is not in the same position.

When I made the statement that Messrs. Wanklyn and Fox had never published a single original experiment, in support of their assertion that the proportion of glycerin yielded by saponification of butter and other fats exhibited no grave departure from the amount required by the accepted view of their constitution, I had in mind the entire absence of original experimental evidence of the kind from the papers read by Messrs. Wanklyn and Fox, in 1883, before the British Association and the Society of Public Analysts. My statement also had reference to the well-known fact that Mr. Fox had made determinations of the proportion of glycerin by a process suggested by Mr. Wanklyn, and that the results of these experiments — for a reason which can only be conjectured — had never seen the light. I had not in my mind the comparatively recently published account of Mr. Wanklyn's solitary experiment, or I should certainly have mentioned it.

On June 6th, at my invitation, Mr. Wanklyn attended a meeting of the Society of Public Analysts, when I read a paper on Saponification, and made in his presence exactly the statement to which he now takes exception. I am sorry he did not, either in the discussion on that paper or in the friendly conversation which occurred between us subsequently, remind me of the omission. I will take care that any prejudice Mr. Wanklyn may have suffered by the omission to mention his experiment shall be remedied at an early date.

With regard to the Chemical Section of the British Association, Mr. Wanklyn need be under no alarm. Only a brief abstract was given at the meeting, as the paper was one of the last on the list for the last day on which the Section met. Mr. Wanklyn well knows what this implies. Hence, on that occasion, I did not actually make the statement to which he takes exception as calculated to mislead, and therefore, as a fact, the Section were not misled by it. The incomplete statement in my paper, as published in these columns, has been duly called to account and corrected by Mr. Wanklyn in this correspondence. I trust this explanation will fully satisfy him, as I am anxious to do him the fullest justice and to avoid any personal friction.

So much for the personal side of the question. The scientific aspect of Mr. Wanklyn's experiment I propose to discuss at an early date. As I have already stated, the published description contains abundant internal evidence of its inconclusive nature.—I am, &c.,

ALFRED H. ALLEN.

Sheffield, Nov. 7, 1891.

Action of Benzoic Acid upon Oil of Turpentine. —G. Bouchardat and J. Lafont.—The action of benzoic acid upon turpentines at 150° affords a practical means of reproducing the camphenols and iso-camphenols.—*C. R.*

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxiii., No. 17, October 26, 1891.

On a New Mineral Species, Boleite.—M. Mallard and E. Cumenge.—The mineral in question is obtained near Santa Maria in Lower California. It is a copper and silver ore of the composition—

$$3[PbCl(HO)CuCl(HO)]+AgCl.$$
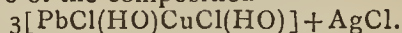
It is found in cubic crystals of a fine indigo blue, accompanied by anglesite, phosgenite, cerusite, and atacamite.

On Bromostannates.—M. Leteur.—The bromostannates of the alkaline metals and of magnesium are yellow and well-crystallised. The anhydrous bromostannates, those of potassium and ammonium, remain unchanged except in very damp air, but the others are very deliquescent. Their concentrated solutions may be heated without decomposition, but if diluted they become turbid and deposit stannic hydroxide with formation of hydrobromic acid. Alcohol decomposes them slowly in the cold, more rapidly in heat. Benzene has no action upon them. The general method for the preparation of these compounds is to mix the concentrated solutions of the two bromides and to evaporate the mixture in a vacuum or in dry air. The author has obtained and described the salts of ammonium, sodium, lithium, and magnesium.

New Crystalline Ferric Oxychlorides.—G. Rousseau. —The highly concentrated solutions of ferric chloride, containing more than 80 per cent Fe_2Cl_6, if kept for some time at temperatures between 160° and 220°, give rise to a crystalline ferric oxychloride, $2Fe_2O_3,Fe_2Cl_6,3H_2O$. This compound, on prolonged contact with boiling water, is converted into ferric hydrate (Fe_2O_3,H_2O), completely isomorphous with the original oxychloride. The author has studied the decomposition of solutions of ferric chloride at temperatures above 220°. In the interval between 225° and 280° there were obtained lamellæ of a brownish red, much more bulky than those of the hydrate above described, agreeing in composition with those of the anhydrous oxychloride, $2Fe_2O_3,Fe_2Cl_6$. Between 300° and 340° there appear large laminæ of a brownish black, $3Fe_2O_3,Fe_2Cl_3$, a new oxychloride. It is probable that at temperatures above 350° we should obtain a series of new oxychlorides of the type $(Fe_2O_3)''Fe_2Cl_6$, in which the proportion of Fe_2O_3 would increase regularly with the heat.

Determination of Thallium.—H. Baubigny.—(See page 239).

Solution of Bismuth Chloride in Saturated Solutions of Sodium Chloride, and on Basic Bismuth Salicylate. — H. Causse. — Sodium chloride, like sal-ammoniac, opposes the dissociating action of water upon the salts of bismuth, and by substituting itself for the free acid contained in bismuth solutions it permits the complete neutralisation of the acid, which may be completely converted into bismuth chloride. The author applies his researches to the preparation of basic bismuth silicylate.

Formation of Quaternary Ammonium Iodides by the Action of Trimethylamine in a Concentrated Aqueous Solution upon the Hydriodic Ethers of Certain Primary Alcohols and of a Secondary Alcohol.—H. and A. Malbot.—There are three different modes of reaction between amines and others. There is *progression* when a new alcoholic radicle is fixed upon the nitrogen; the ether then simply unites with the amine. There is *stagnation* when the nitrogen simply preserves the radicles already fixed; the ether and the amine unite, with elimination of the diatomic carbide

which enters into the ether. In this manner the amine is reproduced in the state of a salt, which may be characterised as simple reproduction. There is *retrogression* when the nitrogen loses one of its radicles originally fixed; the ether and the amine unite, each losing a mol. of its fundamental carbide. From the totality of the experiments described it appears that whenever the affinity of an amine for an ether is sufficient there ensues a simple union of the two. If this combination takes place integrally in the cold it also takes place integrally in heat. If therefore with certain systems (very numerous) of ethers and amines there is not simple union, but union with elimination of carbides, this elimination is not due to the decomposing action of heat upon the ether, but to a reaction of a new order which is set up between the ether and the amine, and which corresponds to a greater development of energy.

A Characteristic Difference between Substituted Alcoholic Radicles connected respectively with Carbon and Nitrogen.—C. Matignon.—The author arrives at the law that the substitution of an alcohol radicle linked to nitrogen increases the heat of combustion more than the substitution of the same radicle if linked to carbon.

New Albumenoid Substance in the Serum of Human Blood.—C. Chabrié.—The author finds in serum a principle distinct from paraglobuline and serine. This compound is present in the blood both of healthy and diseased persons. The author proposes to call it albumone.

Journal fur Praktische Chemie.
New Series, Vol. xliii., No. 11.

Action of Hypochlorous Acid upon Monobromquinolines: Bromcarbostyrile and Dibromquinoline. —Ad. Welter.—The author describes the preparation and properties of parabromcarbostyril, and para-α-dibromquinoline, of meta-bromcarbostyril, of meta-α-dibromquinoline, ana-bromcarbostyrile, and ana-α-dibromquinoline.

Researches from the Laboratory of the University of Freiburg.—These comprise a paper by Ad. Claus, and H. Howitz on the halogen alkylates of para-oxyquinoline and the quaternary ammonium hydroxides derived from them by the action of alkalies; and a memoir by Ad. Claus on the mixed fatty aromatic ketones and their oxidation by potassium permanganate.

Calorimetric Researches by F. Stohmann. — The 24th treatise by the authors on the hydration of closed rings.

Revue Universelle des Mines et de la Metallurgie.
Series 5, Vol. xv., No. 1.

Certain recent Discoveries in the Great Chemical Industries.—H. Martin.—The author summarises the present condition of the alkali manufacture. He admits that the Solvay process does not admit of the industrial production of chlorine or hydrochloric acid. The Deacon chlorine process he considers has had its hour of celebrity, but is now abandoned. The utilisation of HCl is now threatened by the attempts to obtain chlorine from the magnesium chloride thrown off as a waste product at Stassfurt. On the Chance process for the recovery of sulphur from vat-waste he pronounces no decided opinion. On the use of gaseous fuel the author quotes a recent memoir by Prof. Lunge.

MEETINGS FOR THE WEEK.

WEDNESDAY, 18th.—Society of Arts, 8. Opening Address of the 138th Session by Sir Richard Webster, M.P.
THURSDAY, 19th.—Chemical, 8. " On Colour Photometry," by Capt. W. de W. Abney, F.R.S.
FRIDAY, 20th.—Physical. " A New Theory concerning the Constitution of Matter," by Dr. C. V. Burton.

THE CHEMICAL NEWS.

VOL. LXIV., No. 1669.

CHESTNUT-WOOD TANNIN.*

By Prof. HENRY TRIMBLE.

THE *Castanea vesca* of Linnæus or *C. Sativa* of Miller, variety *Americana*, is a large tree of rapid growth found in many parts of the United States, especially in the eastern section, from Maine to Delaware, and on mountains as far south as northern Alabama.

An extract of the wood and bark has been prepared in this country and France for a number of years. This extract is especially useful in tanning, where it corrects the reddish colour of hemlock, and in dyeing, where it gives a dead black with salts of iron. It must not be confounded with the extract of chestnut oak, *Quercus prinus*, Linnæus, which is also largely manufactured in this country, and, no doubt, the manufacturers are not very particular to keep the two separate.

Most of the literature on the subject of chestnut tannin refers to that from the horse chestnut, *Æsculus Hippocastanum*.

In order to leave no room for doubt about the origin of the tannin described in this paper, the chips, free from bark, were collected from a large tree about forty years' old, cut in the month of August.

A summary of the constituents of the wood, as found by a proximate analysis, may be of interest before commencing a description of the tannin :—

	Per Cent.
Crystalline wax, melting at 50° C., soluble in hot 95 p.c. and in absolute alcohol ..	1·03
Gallic acid	0·05
Resin	0·28
Tannin, extracted by absolute alcohol ..	3·42
Mucilage..	1·15
Dextrin .. .. .. , ...	1·89
Sugar.	0·96
Tannin, extracted by water	1·92
Pectin and albuminoids	1·46
Extractive, dissolved by dilute acid	2·95
Ash	7·08
Moisture..	7·05
Cellulose and lignin	70·76
	100·00

It is not certain that the gallic acid pre-existed in the wood, because it may have been formed during the drying of the chips, since the analysis was not made for some time after they were cut and ground.

A special determination of tannin on a separate portion of the wood by gelatin and alum and by permanganate and hide powder gave, respectively, 7·86 and 7·85 per cent.

The tannin used in the following experiments was prepared by percolating 2½ kilos. of the finely powdered wood with a commercial ether, which consisted of about 74 parts ether, 26 parts alcohol, and a small quantity of water. The ether was recovered from the percolate by distillation and the residue dissolved in cold water. The filtered aqueous solution was precipitated in three portions by lead oxyacetate, the precipitates decomposed by hydrogen sulphide, the latter removed by distillation under reduced pressure, and the solution after cooling agitated with ether, which extracted gallic acid from each of the three fractions. The tannin solution from the middle

fraction was warmed to remove ether and then saturated with common salt. An abundant separation of tannin took place, which was collected, washed with a saturated solution of salt, and dried over sulphuric acid in a vacuum.

The dry residue was dissolved in ether-alcohol, filtered and rapidly evaporated to dryness under diminished pressure, which left the tannin in a porous, light red mass This was used for some of the qualitative tests, but for many of the reactions the tannin was further purified by again precipitating in three fractions with lead oxyacetate, the lead removed by hydrogen sulphide, the latter removed by distillation under reduced pressure until the liquid had reached a small bulk, when it was agitated with ether, which removed gallic acid from each of the three fractions. The aqueous solution was then distilled to dryness under reduced pressure, the residue in each case dissolved in ether-alcohol, filtered, and rapidly distilled under the same circumstances to dryness, which left the tannin in a nearly white porous mass completely soluble in cold water.

In physical and chemical properties this chestnut-wood tannin so closely resembled gallotannic acid that the following comparative statement is given, to show both the character and resemblance at once :—

Reagent.	Chestnut-wood tannin.	Gallotannic acid.
Ferrous salts.	No change.	No change.
Ferrous chloride and Ammonium hydr.	Blue-black ppt.	Blue-black ppt.
Tartar emetic and Ammonium chloride.	Purple ppt. Slight clouding. Pale ppt.	Purple ppt. Slight clouding. Pale ppt.
Copper sulphate and Ammonium hydr.	No ppt. Light brown ppt.	No ppt. Light brown ppt.
Bromine water.	No ppt.	No ppt.
Calcium hydrate.	White ppt. turning light blue.	White ppt. turning light blue.
Amm'ium molybdate.	Yellow colour.	Yellow colour.
Sodium sulphide.	No change.	No change.
Conc. sulphuric acid.	Light yellow.	Light yellow.
Sulphuric acid (1—9).	No deposit.	No deposit.
Lead nitrate.	White ppt.	White ppt.
Cobalt acetate.	Flesh-colored ppt.	Flesh-colored ppt.
Manganese acetate.	White ppt.	White ppt.
Uranium acetate.	Crimson colour, turning dark red.	Crimson colour, turning dark red.
Ammonium picrate.	No ppt.	No ppt.
Potassium bichromate.	Brown ppt.	Brown ppt.
Ferric acetate.	Blue-black colour and ppt.	Blue-black colour and ppt.
Alkaloids.	White ppt.	White ppt.
Gelatin.	White ppt.	White ppt.
Lead acetate.	Light ppt.	Light ppt.

One per cent solutions of the tannins were used as recommended by Procter (" Text Book of Tanning," p. 112), and all the reagents were applied in solution except sodium sulphide. These reactions do not all agree with those given by Procter, but he used a solution of commercial extract of chestnut which may have consisted in part or entirely of chestnut oak, or the difference may be due to the non-tannin constituents of the extract.

The chestnut-wood tannin was found to decompose, when heated to 200° C., into pyrogallic and metagallic acids, an abundant crop of crystals being obtained of the

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former. Each of the three fractions was estimated for sugar, and the first found to contain 10·48, the second 7·98, and the third 6·18 per cent of glucose, which no doubt had existed as a glucoside.

The second fraction was dried at 120° C. and submitted to elementary analysis as follows :—

Substance.
(1) 0·1179 grm. gave 0·2211 CO_2 and 0·0486 H_2O.
(2) 0·0843 „   0·1575 CO_2 and 0·0363 H_2O.

	I.	II.
C	51·15	50·95
H	4·58	4·79
O	44·27	44·26
	100·00	100·00

On calculating for the presence of 7·98 per cent glucose and deducting the difference from (1) we get :—

	Found.	Calculated for $C_{14}H_{10}O_9$.
C	52·11	52·17
H	4·40	3·10
O	43·49	44·73
	100·00	100·00

It will be noticed that the percentage of hydrogen is greater than that in digallic acid, but in view of the fact that it was dried at 120° C. instead of 140° C., as recommended by Löwe (*Zeit. fur Anal. Chemie*, vol. xi., 378), and that it agrees so closely with gallotannic acid in all its reactions, we cannot but conclude that it is gallotannic acid.

An acetyl derivative was prepared which in many respects resembled pentacetyl tannin, but the figures proving it could not be obtained in time for this paper.

A METHOD OF STANDARDISING IODINE SOLUTION FOR THE DETERMINATION OF SULPHUR IN STEEL AND PIG-IRON.

By J. M. WILSON.

I DESIRE to call attention to a method of standardising iodine solution, for use in titrating sulphur in iron and steel, which has been in use in the laboratories of some of the iron works of the Ohio Valley for the past four years, and which, I believe, I was the first to use, in the laboratory of the Laughlin and Junction Steel Co., at Mingo Junction, Ohio.

Finding the hyposulphite method would occasionally fail and frequently gave non-concordant results, on doubling quantities, I cast about for a substitute, and at length settled on a steel the sulphur contents of which had been very carefully determined by *all* the known evolution methods as a standard.

By using this standard steel I standardised my iodine solution by the same process that I used to determine the unknown percentage of sulphur in the samples of pig-metal and steel submitted for analysis, avoiding the objections raised by certain chemists, that the hydrocarbons evolved with the hydrogen sulphide interfered with the titration by iodine when KOH was used as an absorbent; for the iodine solution being standardised under conditions of actual working, it is to be presumed that, inasmuch as all the C in our standard steel is combined, there will be as much hydrocarbon evolved therefrom as from any sample we may have submitted to us for determination.

As to accuracy, there can be no question on that score, the only essential being that we make sure of complete solution of the metal under treatment by taking plenty of

time to *complete the solution* of the *difficultly soluble sulphides, &c.*, which invariably accompany high sulphur irons, and making sure of absorbing *all* the evolved H_2S.

It is sufficiently rapid to suit the most fastidious, as it requires no more time than is required to make the sulphur determination in the ordinary routine of laboratory work.

Below I add a few comparative results obtained in the course of work about a busy steel plant laboratory, and which are not picked, nor were they made for the purpose of establishing the method of standardising, as that had been in use almost four years before these results were obtained, but were made for the purpose of convincing the president of a certain furnace company that our method of sulphur determination was accurate and comparable with that used by his chemist.

The determinations by the iodine method were made by my assistants, those by Br and HCl by myself.

	By Iodine.		By Br and HCl.	
Car 2238.	0·067 p. cent S.		0·063 p. cent S.	
„ 2238. 2nd sample.	0·060 „ „		0·064 „ „	
„ 3614.	0·069 „ „		{ 0·072 „ „	
			0·071 „ „	
„ 4326.	0·080 „ „		0·075 „ „	
„ 4326. 2nd sample.	0·069 „ „		{ 0·064 „ „	
			0·063 „ „	
„ 8113.	0·073 „ „		{ 0·068 „ „	
			0·068 „ „	

The above are all the comparative determinations made at that time, October and November, 1890.—*Journal of Analytical and Applied Chemistry*, August, 1891.

ELECTROLYTIC DETERMINATION OF METALS AS AMALGAMS.[*]

By G. VORTMANN.

(Concluded from p. 242.)

Separation of Lead in Alkaline Solutions.

LEAD may be also quantitatively eliminated as an amalgam from an alkaline solution. The salt of lead is dissolved in water along with mercuric chloride, a few grms. of tartaric acid are added and then an excess of soda-lye. There is produced a brown precipitate which readily dissolves on the addition of potassium iodide. The liquid is diluted with water as far as the size of the capsule permits, and the electric current is passed through. The lead is entirely separated out as an amalgam without the formation of peroxide. The electrolysis is completed as soon as a sample of the liquid shows a pure white turbidity on the addition of ammonium sulphide.

The amalgam must be washed with water only, as alcohol occasions loss. In order to dry the amalgam as rapidly as possible it is washed several times with hot water, allowed to drain, and dried in a current of air; as it is quickly oxidised whilst moist, the results obtained are in general too high, so that this process may be recommended for the separation of lead from other metals (tin and arsenic), but not for determination.

For the separation of lead from other metals (tin, antimony, arsenic) its precipitation from an ammoniacal solution will be very suitable, though a part appears as peroxide. I mixed the solution of lead nitrate and mercuric chloride with tartaric acid, then with ammonia in excess, and conducted the electric current through the liquid until a specimen remained clear on the addition of ammonium sulphide. The lead was chiefly deposited as amalgam, but a small quantity appeared as peroxide at the positive electrode; I decanted off the liquid, washed both electrodes with water, put in the platinum capsule a solution of sodium acetate, acidified with acetic acid and

mixed with sodium nitrite, and passed the current through until lead could no longer be detected in the liquid. The ammonia was then washed and dried as recommended above.

On the electrolysis of the ammoniacal solution the lead amalgam was partly deposited in a spongy form, though strongly adherent. On the electrolysis of the acetic solution the spongy mass gradually disappeared entirely, and the amalgam finally formed a uniform mirror-like surface. This experiment showed plainly that in order to obtain a uniform amalgam on the electrolysis of ammoniacal solution the quantity of mercury present must be greater than on employing an acid solution. The same fact was observed in the case of zinc and bismuth.

Determination of Bismuth.

The separation of bismuth as an amalgam is best effected by means of acid solutions. The double ammonium oxalate is not well suited for its determination, because bismuth oxalate is much too sparingly soluble in the solution of ammonium oxalate. In order to prevent the precipitation of basic salts there must always be present a moderate excess of free acid, which again must be avoided from various reasons; for in presence of much free nitric acid there is formed at the positive electrode a larger quantity of bismuth peroxide, and the complete separation of the metals is effected less easily. They must, if possible, be washed without interrupting the current. In presence of much free hydrochloric acid there ensues at the positive electrode a strong development of hypochlorous acid, which is very annoying to the operator. I avoided the use of a large excess of hydrochloric acid by the addition of potassium iodide, when the bismuth iodide, which is deposited at first, re-dissolves in the excess of potassium iodide to an orange-yellow clear liquid, which may be diluted with water without any deposition of basic salts. A second method of avoiding too large an excess of free acid (in case of hydrochloric solutions) consists in diluting the liquid not with water but with ethylic alcohol, since both mercuric chloride and bismuth chloride are readily soluble in alcohol, and the solution remains perfectly clear even on addition of a large quantity of alcohol.

For the confirmatory analyses there was used pure bismuth oxide (calculated as 89·69 per cent bismuth), which I obtained partly by igniting basic bismuth nitrate, partly by oxidising metallic bismuth with nitric acid. Professor Dr. A. Classen kindly placed at my disposal the purest metallic bismuth which he has obtained for the determination of its atomic weight, for which I here express my best thanks.

1. *Separation of Bismuth from a Solution of Potassium Iodide.*—Bismuth oxide, along with a weighed quantity of mercuric chloride, was dissolved in hydrochloric acid in the platinum capsule; solution of potassium iodide was then added until the precipitate formed at first was re-dissolved, and the liquid was diluted as far as possible with water. On the electrolysis of this liquid the bismuth amalgam separated out very well, whilst the free iodine collected on the surface in the form of a mass filled with bubbles. When a sample of the liquid remained perfectly clear after the addition of ammonia and ammonium sulphide, I poured, without interrupting the current, a few c.c. of concentrated soda-lye into the capsule until the iodine was entirely dissolved, and continued passing the reinforced electric current for an hour until a sample of the liquid, after the addition of sodium sulphite (in order to reduce the iodate) and ammonium sulphide, no longer gave a brown colouration. The amalgam was then washed and dried in the ordinary manner.

Bismuth amalgam, if sufficient mercury was used, is of silvery metallic lustre; if the quantity of mercury was too small it is covered with a blackish brown layer of amorphous bismuth, which adheres so firmly that nothing is lost on cautious rinsing. The amalgam is stable in the air; the weight does not vary after several days'

preservation in the exsiccator or even in the open air. If heated for three hours in the air-bath at 90° neither its weight nor its appearance is altered.

2. *Separation of Bismuth from a Hydrochloric Solution mixed with Alcohol.*—The mixture of bismuth oxide and mercuric chloride was dissolved in hydrochloric acid; the solution was mixed with about 50 c.c. of alcohol at 96 per cent, mixed by stirring with the positive electrode, and water was gradually added, with constant stirring, until the surface of the liquid was at least 1 c.m. below the margin of the capsule, when the electric current was introduced. It is not advantageous to dilute the solution of the chlorides exclusively with alcohol, since an alcoholic solution is much disposed to creep over the edge of the capsule, thus occasioning loss. If we use a mixture of alcohol with two volumes of water, creeping does not occur. The bismuth amalgam is uniformly deposited as a mirror-like surface, whilst acet-aldehyd and its chlorine substitution products are formed at the positive electrode. As soon as a sample of the liquid remains clear on the addition of ammonia and ammonium sulphide the liquid is decanted off, and the amalgam is quickly washed in the usual manner. In some cases the author has neutralised the free acid by an addition of soda-lye before decanting off the liquid.

Both the above methods give good results, whether the bismuth is present in a small or a large quantity. In presence of much bismuth, however, the second method is preferable, as according to the former method a large quantity of potassium iodide would be required for the formation of the double salts, which involves the separation of an unpleasantly large quantity of iodine in electrolysis.

3. *Separation of Bismuth from Nitric and Ammoniacal Solutions.*—Bismuth may also be separated as an amalgam from a nitric solution, but the relative proportion of mercury must be much larger (to 1 part of bismuth at least 4 parts of mercury). The formation of bismuth peroxide is avoided by the addition of tartaric acid. I dissolved bismuth and mercuric oxide in nitric acid, added tartaric acid, and diluted with water. The amalgam obtained on electrolysis was washed and dried in the usual manner. The mercuric oxide contained 92·076 per cent of mercury.

From an ammoniacal solution mixed with tartaric acid bismuth may likewise be completely deposited as an amalgam; but here, as in the case of a nitric solution, much mercuric chloride must be used, as the bismuth is otherwise in part deposited in the form of an amorphous blackish brown powder which can scarcely be washed in water without loss. I should therefore not recommend the separation of bismuth as an amalgam from an ammoniacal solution for its determination, but merely for its separation from other metals (*e.g.*, tin, antimony, and arsenic).

It is well known that the electrolytic determination of antimony presents peculiar difficulties, and that a good adhesive deposit is obtained only by means of careful work, and, according to Prof. Classen, in presence of not more than 0·16 grm. of antimony. The solubility of mercury in solution of sodium sulphide, and the ease with which this metal is precipitated electrolytically, made it *à priori* likely that the determination of antimony as an amalgam would be readily practicable. In fact it presents no difficulties. About 2 parts of mercury must be present in solution to 1 part of antimony; a larger proportion of mercury is not injurious, and it is even advantageous if the quantity of antimony is large. As mercurial salts are reduced by antimony oxide in alkaline and sulph-alkaline solutions with separation of metallic mercury, the antimony must always be present in the form of pentoxide. I dissolved a mixture of tartar emetic and mercuric chloride in hot water, with an addition of strong bromine water, until the solution when completely effected was coloured yellow by free bromine. I then added the solution of sodium sulphide mixed with sodium hydroxide (as

indicated by Prof. Classen) until the precipitate formed at first was re-dissolved. The solution was then diluted with water as much as the size of the platinum capsule allowed, and the electric current was introduced. Here also, as in the determination of mercury alone, a small quantity of black mercury sulphide was deposited at the positive electrode, which disappeared again towards the end of the operation, so that the positive electrode was ultimately coated with a thin layer of yellow sulphur. When a sample of the liquid, on the addition of dilute sulphuric acid, gave a pure white milky precipitate, the liquid was poured off and the amalgam was washed and dried in the ordinary manner.

Antimony amalgam has a steel-grey colour and is permanent in the air; it dissolves completely in a mixture of tartaric acid and dilute nitric acid, generally leaving upon the capsule a very thin stain of platinum black. The separation of antimony has the advantage that large quantities can be separated at pleasure, if only the vessel in which the electrolysis is performed is sufficiently capacious. As tin, when present as oxide, can be electrolytically deposited neither from a concentrated alkaline solution nor from an alkaline sulphide, the amalgam method will probably be very suitable for separating tin from antimony.

If an ammoniacal solution of antimony mixed with tartaric acid is submitted to electrolysis, no antimony is deposited. This non-precipitability of antimony from an ammoniacal solution will probably be very useful for its separation from lead, bismuth, and other metals.

Separation of Arsenic as an Amalgam.

My experiments for the electric determination of arsenic as an amalgam have hitherto proved fruitless. The arsenic escapes entirely, or in part, as arsenic hydride.

The author is continuing his experiments on this method of separating different metals, and reserves to himself its further development.

DETERMINATION OF SMALL QUANTITIES OF ALKALI AND RECOGNITION OF THE NEUTRALITY OF WATER.

By F. MYLIUS and F. FOERSTER.

ALTHOUGH here (perhaps from a trace of iron present in the zinc sulphate) the solubility of the solution seems imperfect, it appears from the experiment that, by means of our process, 0·002 per cent of free zinc oxide or of free sulphuric acid may be detected in crystalline zinc sulphate. In case of zinc salts, methyl orange is generally used as indicator for the detection of free acid. When this colouring-matter was used it was possible to add to a solution of 5 grms. zinc sulphate 100 c.c. N/1000 sulphuric acid without completing the change from the yellow to the red colour.

Solutions of zinc chloride may also be satisfactorily neutralised by means of the eosine reaction, or their percentage of neutral salt may be determined. In an apparently neutral solution of this salt the proportion of Zn : Cl was found 1 : 2·01.

Whilst in the salts of magnesium, cadmium, manganese, nickel, and cobalt, the reactions are like those of zinc, the oxide salts of iron, aluminium, and chrome behave with eosine like free acids. Lead and silver yield, with iodeosine, salts of a fine violet colour; they are insoluble in water, whereby the use of eosine in testing the salts of these metals is rendered more difficult.

Lest iodeosine should appear as a universal indicator, it must be pointed out that it is unsuitable for the determination of organic acids. The determination even of oxalic acid with millenormal alkali gives no quite accu-rate values; with the weaker acids, such as acetic or formic acid, titration with eosine is impracticable, as there occurs no distinct change of colour.

Colorimetric Determination of Alkali.

Titration with millenormal solutions permits us to determine in 100 c.c. of water quantities of alkali equivalent to 0·1 m.grm. Na_2O. For smaller proportions the method above mentioned may be modified into a colorimetric process. Such determinations, which are much used in other branches of analytical chemistry when the estimation of "traces" comes into question, have hitherto not been employed in alkalimetry. With the aid of iodeosine we may obtain a colorimetric method for alkalimetry on the bases of the following facts:—If a very dilute aqueous solution of alkali is shaken up with an ethereal solution of eosine, the eosine being in excess with reference to the alkali, the solution of the alkali takes a more or less intense rose-colour in proportion to the quantity of alkali present. From the intensity of the rose-colour obtained we may infer the quantity of alkali present in the solution. For this purpose it is necessary to operate in a strictly definite manner. We have to attend to the purity of the water and the eosine to be used, and the proportion of colouring-matter in the ethereal solution, and the volumes of the two liquids which come into contact. All the vessels employed must be of the best quality of glass, lest an error might arise from alkali taken up during the operation.

The conditions to be observed in the colorimetric process follow from the behaviour of iodeosine and its alkaline salts with water and ether.

On the ground of the complete precipitability of the colouring-matter from its alkaline solutions by acids, we are tempted to draw the conclusion that free eosine is insoluble in water, which would explain the slow change of colour on neutralisation from the hydrolytic splitting up of the alkaline salt. But this inference is inadmissible; free eosine is soluble to a slight extent in pure water, with the same rose-colour which appears in a dilute alkaline solution. No difference between the alkaline and the aqueous solutions can be perceived either on examination with the naked eye or on the observation of the absorption spectrum. The red colour remains even when a small quantity of acid is added to the aqueous solution. The colour disappears only on the addition of a large excess of acid, when the colouring-matter is precipitated in orange-yellow flocks.

We have here evidently to do with two modifications of eosine. As the yellow precipitated iodeosine is anhydrous, the assumption is natural that the red soluble modification is a hydrate, which is converted into the yellow anhydride by dehydrating agents, such as acids. This agrees with the circumstance that the yellow solutions of the colouring-matter in alcohol or acetone turn the redder the more water is added to the solution. It is also known that the alkaline solutions when highly concentrated have a yellower tone than when dilute. In support of this view it may be stated that in the fluoresceines the two modifications—the hydrate and the anhydride—may be isolated at pleasure. We must not omit to point out that, even without the above assumption, the facts observed can be satisfactorily explained on the basis of the electrolytic theory of dissociation and its consequences.

The red solution of iodeosine hydrate in water is decolourised by shaking up with a relatively large quantity of ether. Although aqueous ether has a much greater solvent power for the colouring-matter than has water, yet the latter, if shaken up with an ethereal solution of eosine, takes up a little eosine and assumes a red colour. The quantity depends on the proportions of the three active substances, and is constant if the conditions remain unaltered.

The rose-colour of the dissolved alkaline eosinates decreases in intensity proportionally to their dilution. It

is not affected, at least in high solutions, by the presence of an excess of alkali or of neutral salts.

As in a colorimetrical determination the ethereal solution of eosine is in excess with reference to the alkali, there arises the question whether under such conditions we have the formation of neutral or acid salts. Experiment shows that neutral salts only are formed · 0·4014 grm. iodeosine was dissolved in a slight excess of decinormal soda-lye; the solution, with occasional shaking, was mixed with ether and so much decinormal sulphuric acid that the first trace of eosine passed into the ether; a further quantity of acid caused then at once a corresponding quantity of eosine to pass into the ethereal solution. It appeared that the alkali combined with the eosine had been furnished by 9·7 c.c. of decinormal solution, and consequently that the salt $C_{20}H_6Na_2I_4O_6$ had been formed, whilst the acid salt, $C_{20}H_7NaI_4O_5$, would require only half as much. Hence it follows that the acid salt is not permanent in an aqueous solution in presence of ether, but is at once resolved into the neutral salt and free eosine.

The other alkalies behave like soda. Hence, from the quantity of the dissolved eosine, the quantity of the alkali present in the solution and combined with the eosine should follow in the most simple manner. But this is not exactly the case.

We have found that dilute alkaline solutions withdraw rather less colouring-matter from the ethereal solution of eosine than would be required for the formation of the neutral salt. We explain this circumstance by the fact that even the neutral alkaline salts of iodeosine are not perfectly permanent in water, and, in consequence of the slight decomposition caused by the water, they give off a small quantity of free eosine to the ether.

According to our experiments sodium eosate is not taken up by ether.

(To be continued.)

ON THE MUTUAL REACTION OF FERRIC SALTS AND SOLUBLE SULPHO-CYANIDES.

By GERHARD KRÜSS and HERMANN MORAHT.

THE pamphlet before us is a reprint from Liebig's *Annalen der Chemie.*

From the author's researches it appears that on mixing ferric salts with an excess of potassium sulphocyanide there is always formed a double salt containing 9 mols. of potassium sulphocyanide.

If to an excess of ferric salt there is added but little potassium sulphocyanide it is perhaps possible that free ferric sulphocyanide is present in the solution; still this is not probable, as the double compounds of ferric sulphocyanide with the alkaline sulphocyanides are more permanent than the former alone.

If a solution of the iron salt is diluted with distilled water in a beaker until the liquid has only a faint yellow tint, and if a concentrated solution of alkaline sulphocyanide is then added, there appears at once the deep cherry-red colour of the double sulphocyanide of the formula—

$$Fe(CNS)_3.9\overset{1}{R}CNS+4H_2O.$$

ON THE SULPHO-SALTS OF VANADIUM.

By GERHARD KRÜSS and KARL OHNMAIS.

THIS memoir has been reprinted in a separate form from Liebig's *Annalen der Chemie.*

We notice the methods which have been used for the determination of vanadium. The sulpho-salts, on igni-

tion in the air, yield vanadium pentoxide, which can be weighed as such.

The ammonium salt is heated in a covered porcelain crucible until the sulphur and the ammonia are expelled; it is then ignited with excess of air until the weight is constant, which is generally effected in an hour, and may be accelerated by passing oxygen over the fused mass. An addition of ammonium nitrate is not recommended, as loss may be readily occasioned be spirting.

The determination of vanadium in salts with fixed alkalies was first effected by a volumetric method depending on the reduction of the acid solution of a vanadiate to vanadium tetroxide by means of sulphurous acid, and subsequent oxidation of the tetroxide to vanadic acid by solution of permanganate. More recently the authors have adopted the method which C. Friedheim has proposed for the separation of tungstic and vanadic acids.

ON THE OCCURRENCE OF NITROGEN IN URANINITE, AND ON THE COMPOSITION OF URANINITE IN GENERAL.*

By W. F. HILLEBRAND.

Analyses of Uraninite.

THE analyses which follow were, with two exceptions, V. and XVIII., made before recognition of the nature or importance as regards quantity of the gas given off by acid, and, as before said, their object was chiefly to ascertain the relative percentages of UO_2, UO_3, and rare earths with a reasonable degree of accuracy.

The specific gravities of the Connecticut mineral were so much higher than any published that considerable care was exercised in their verification and in all subsequent determinations. The figures given represent the density of the mineral dried at 100° C., for the small amounts of hygroscopic moisture, varying as they did with different specimens, would exert a marked effect on the result if included.

A knowledge of the condition of the iron, which all analyses show accompanies uraninite in small quantity, is of prime importance for the correct volumetric estimation of UO_2. Comstock and Blomstrand have both assumed that it exists in the ferrous condition, and from the oxygen transferred in titration have deduced a corresponding amount before calculating UO_2. While not in a position to deny the correctness of this assumption for a portion of the iron at least, I have, with one or two exceptions which will be noted in due order, preferred to consider all iron dissolved by dilute nitric acid as ferric oxide, and for the following reason:—The matter insoluble in dilute nitric acid may consist of columbite, felspar, quartz, mica, a very sparingly soluble phosphate, and the reddish infiltration matter filling the minute seams in the mineral, substances which it is practically impossible to remove entirely from any sample containing them. When the uraninite is dissolved this insoluble matter is decidedly red (unless columbite predominates largely) from ferric oxide, of which it is probable the infiltration matter is largely composed. In all such cases a large percentage of the insoluble matter is ferric oxide, and only in one case could any ferrous oxide be found in it aside from that belonging to columbite. It was further noticed that more iron was found in solution, and correspondingly less in the insoluble, when the heating had been prolonged beyond the usual time or when a stronger acid was employed. It seemed therefore certain that a portion of the iron in solution had been derived from

TABLE I.—*Uraninite from Glastonbury, Connecticut.*

	I. a.	I. b.	I. Mean.	II.	III.	IV.	V. a.	V. b.	V. Mean.
UO$_3$	—	—	22·08	23·35	22·22	(e)26·48	23·13	22·94	23·03
UO$_2$	59·09	59·17	59 13	58·01	(c)59·31	(f)57·43	—	—	(g)59·93
ThO$_2$	}9·09				}9·78	9·79	10·01		
CeO$_2$						0·25	0·29		
ZrO$_2$?	—	}9·50	9·57	—	}10·31	—	0·15	}11·13	11·10
(LaDi)$_2$O$_3$	}0·55				}0·46		0·13	0·15	
(YEr)$_2$O$_3$							0·20	0·48	
PbO	3·14	—	3·14	3·24	3·07	3·26	3·08	3·08	3·08
CaO	0·08	—	0·08	—	undet.	0·08	0·17	0·04	0·11
MgO	—	—	—	—	undet.	—	—	—	—
Alk	—	—	—	—	undet.	trace	—	—	—
H$_2$O	0·97	—	0·97	undet.	undet.	0·61	0·43	0·42	0·43
N	undet.	undet.	undet.	undet.	undet.	undet.	—	—	(h)2·41
Fe$_2$O$_3$	(a)1·21	—	1·21	0·33	(d)0·67	0·40	0·28	0·29	0·29
MnO	—	—	—	—	—	trace	—	—	—
SiO$_2$	1·06	—	1·06	—	0·25	0·16	0·15	0·18	0·16
P$_2$O$_5$	—	—	—	—	—	—	0·02	—	0·02
Fl	—	—	—	—	—	—	0·04	—	0·04
Insol.	0·85	—	0·85	(b)1·74	0·42	0·70	0·85	0·92	0·89
Cb$_2$O$_5$	0·96	—	0·95	—	—	—	—	—	—
Total	—	—	99·05	96·91	96·25	99·49	—	—	101·49
All U as UO$_2$	—	—	79·98	80·06	80·29	82·43	81·75	81·59	81·67
Sp. gr.	—	—	9·139	9·051	—	9·587	—	—	9·622
Temp. °C.	—	—	17½	21	—	21	—	—	19·4

(a). Estimated by weight; probably contaminated by earths or by alumina. Another fragment gave 0·43 Fe$_2$O$_3$.

(b). Containing 0·55 SiO$_2$, 0·86 Fe$_2$O$_3$, 0·33 Al$_2$O$_3$, &c.

(c). Mean of 59·07, 59·15, and 59·71. Separation by HFl gave 60·05.

(d). Too high, since it was estimated by weight and found to contain some rare earths.

(e). Gravimetrically after separation by HFl there was found 28·58 and 26 89.

(f). Mean of 57·46 and 57·39. Probably too low, and UO$_3$ consequently too high, since they were among the earlier determinations made and no material was left for verification after the method was perfected.

(g). Mean of 59·88, 60·07, and 59·83.

(h). Mean of 2·39 and 2·46 by decomposition with H$_2$SO$_4$ in sealed tubes, and 2·33 and 2·46 by fusion with NaKCO$_3$ in a current of CO$_2$. The first determinations were made in the apparatus shown (see *ante*), and gave 2·14 and 2·21 per cent, but decomposition was incomplete and the percentage was calculated on the assumption that the undissolved residue had the same composition as the portion dissolved, a view hardly tenable in the light of subsequent experiments. They are, therefore, not used in deriving the mean given in the analysis.

ferric oxide of the gangue, and possibly all of it. It was impossible to tell how much, if any, might have existed in the ferrous condition, and therefore it seemed better to count the whole as ferric oxide. In any event the amount found is always so small as to affect the percentage of UO$_2$ but slightly, and never enough to cause trouble in comparing different analyses. That none of the iron belongs to uraninite itself appears from an experiment made upon Glastonbury material (No. V.). When boiled for many hours with dilute hydrochloric acid till 25 per cent of the mineral had dissolved, not a trace of iron was left in the undissolved portion.

Proof is likewise lacking of the state of oxidation of cerium, but CeO$_2$ seems its more natural condition in the presence of other binoxides in overwhelming proportion. As with iron, however, its small amount renders this for purposes of calculation a matter of small importance.

It must be borne in mind that the combined earths are probably too low in all cases except Nos. V. and XVIII., in which two precipitations of nitrates by ether were made to separate the last traces of earth from uranium. It is assumed that separation is then perfect, for by no known means could a further trace be extracted. That an appreciable amount of earths escaped separation in other analyses, and went to increase the apparent percentage of UO$_3$, was at one time shown in working up some of the residues, amounting to 10 or 12 grms., for pure U$_3$O$_8$,

when a considerable weight of earths was obtained, amounting to at least one-third of 1 per cent of the residues.

I. From a large crystal nearly an inch across, which was collected by Prof. F. W. Clarke, the analysis of which led to all subsequent work. It was much contaminated with reddish felspar, quartz, yellow muscovite, and, as examination of the insoluble showed, with columbite, besides a reddish infiltration product lining cracks and becoming apparent on broken surfaces. Most of these were removed, but enough remained to render the analysis in some respects unsatisfactory. The amount of soluble silica indicated thorite as a possible source of the thoria, which the other analyses show cannot be the case. The presence of such an amount of columbic acid in a readily soluble form—for it was obtained by boiling the nitric acid solution of the mineral after filtration from the insoluble matter—points to some columbate other than columbite. Microscopical examination of a thin section of the crystal showed a few cracks filled with a reddish brown and yellow material, part of which was a readily decomposable silicate of some kind, as evidenced by the fuchsine test after treatment with hydrochloric acid and washing with water, but the total visible impurity was very little. A portion of the water undoubtedly belonged to the foreign matter.

II. Obtained from Prof. W. N. Rice, Middletown, Con.

TABLE II.—*Uraninite from Branchville, Connecticut.*

	VI.	VII.	VIII.	Comstock's analysis.
UO_3	13·27	21·54	14·00	40·08
UO_2	72·25	(a)64·72	(b)70·99	54·51
ThO_2.. .. .. }	7·20	6·93 }	6·52	—
ZrO_2? .. .. }		0·33 }		—
PbO	4·35	4·34	4·35	4·27
MnO	0·10	0·07	?	—
CaO	0·18	0·22	0·30	—
MgO .. .. .. }	—	—	0·15	—
Alk.... .. .. }				
H_2O	0·68	0·67	(c) 0·68	0·88
N	undet.	undet.	(d)2·63	—
Fe_2O_3	0·11	0·28	0·27	FeO 0·49
SiO_2	0·03	0·13	0·20	—
Insol...	0·04	0·14	(e)1·40	—
Total	98·21	99·37	101·49	100·23
All U as UO_2 .	84·78	85·06	84·21	—
Sp. gr.	9·733	9·560	9·348	—
Temp. °C ..	27·7	0·30	15·7	—

(a). No material was left for a verification of this figure after perfection of the method of UO_2 estimation : but the low density compared with that of the others when corrected for insoluble matter of 2·7 sp. gr., and the fact that a UO_2 determination by Zimmerman's method (p. 232), in which, however, decomposition was not quite complete, gave 63·28 per cent, point to its correctness.

(b). Mean of 71·11 and 70·87.

(c). Assumed as in VI.

(d). Only enough material for a single estimation was left, and being one of the earliest made it was carried out in the apparatus depicted on p. 245, wherein only 89·7 per cent of the powder had dissolved after about 210 hours, when the experiment was discontinued because of danger of breakage to the flask. The figure here given is calculated on the basis of like composition for the dissolved and undissolved portions,—an improbable assumption in the light of later experiments,—and is probably too low.

(e). The gangue was mainly reddish felspar, and contained 0·31 (or 22 per cent) Fe_2O_3 besides, but only an indeterminable trace of FeO as ascertained in a separate portion. The increase in the percentages of CaO, alkalies, and SiO_2, with progressive increase of insoluble matter, indicates clearly a partial solution of the felspar.

III. Collected by myself as small crystals and fragments. Only a very small amount was available.

IV. Obtained from Mr. E. F. Sheldon, of Middletown, Connecticut.

V. From the same source as No. IV., but at a later date. A very large irregular crystal of this lot was crushed and purified as far as possible, and with this material a very careful analysis, duplicated in part, was made for the purpose of obtaining an accurate summation. This analysis post-dates all others published in this paper except No. XVIII. In addition several estimations of nitrogen were made by the different ways mentioned already, and numerous experiments which it was hoped might throw light upon the ultimate composition of the mineral.

All the above material came from Hales's quarry, in the town of Glastonbury, a few miles north-east of Middletown, Conn.

VI., VII., VIII.—This material was all received from Profs. Brush and Dana, of New Haven, and was the residue of the material from which Comstock had taken his for analysis. No. VI. was by far the purest of any material obtained from any locality, the crystals and fragments being brilliant and well defined and almost absolutely free from impurity. It is earnestly to be hoped that more of this excellent material may be found at Branchville for closer investigation, since it represents the extreme of perfection as regards crystallisation and freedom from attached and infiltrated foreign matter, besides possessing the greatest density and the highest percentage in UO_2 and nitrogen of any known variety.

(To be continued).

PROPERTIES OF PRECIPITATES, &c.*

By E. WALLER, Ph.D.

(Continued from p. 248).

MnO_2 (or MnO_2H_2O, MnO_22H_2O, &c.).

Rem.—For separation in two separate cases. 1. From acetate solution by addition of an oxidising agent, usually Br. 2. From a boiling solution in nitric acid, by addition of crystals of $KClO_3$. Also (3) obtained in titration by the Volhard method—adding standard (volumetric) solution of $K_2Mn_2O_8$ to a solution neutralised by ZnO. In all cases the precipitate probably contains some water of constitution (hydrated oxide).

Cond.—Absence of HCl or other halogen acids, lower oxides of nitrogen or reducing agents. In Case 1, a fair proportion of alkaline acetate must be present, to supply base to the mineral acid which might otherwise be set free. Boiling solution necessary.

Sol.—Dissolved or prevented from forming by dilute mineral acids, particularly HCl. Insoluble in moderately strong acetic or in concentrated nitric. When formed it is soluble in strong HCl, forming temporarily an olive-green solution of Mn_2Cl_6, which becomes practically colourless $MnCl_2$ by heating. Readily dissolved by HCl or H_2SO_4 in presence of reducing agents (SO_2, $H_2C_2O_4$, $FeSO_4$, &c.).

Contam.—Salts of fixed alkalies, Fe_2O_3, ZnO.

Ni (*Electrolytic*).

Rem.—Requires a stronger current than Cu—two or three Bunsen cells (12 to 14 c.c. oxyhydrogen gas per minute). The rapid deposition of the metal is somewhat checked as soon as a coating of nickel has formed, tending to be slower the thicker the coating. This peculiarity is most marked in cold solutions. In preparing for weighing it is treated as electrolysed Cu, by washing with water, then with alcohol, and drying at a gentle heat.

Cond.—Solution should contain no other metals of the $(NH_4)_2S$ or H_2S groups. Chlorides should be preferably absent. The solution should contain the nickel as double ammonium nitrate, sulphate, or oxalate (the latter most advantageously), and excess of ammonia. The operation is more rapid at 70° C. In consequence, ammonia requires to be added from time to time.

Sol.—Dissolves readily in HNO_3, especially with the aid of heat. Slowly soluble in strong solution of $(NH_4)_2C_2O_4$.

Contam.—Co, Fe, and Zn, being precipitated from oxalate solution under the same or similar conditions, may be present in the coat unless previously separated.

$Ni(OH)_2$ and $Ni_2(OH)_6$.

Rem.—Usual precipitant, KOH or NaOH. If the solution contains free halogens, or hypochlorites, hypobromites, &c., $Ni_2(OH)_6$ may be precipitated *black*. The most marked characteristic of the precipitate is the per-

* From *School of Mines Quarterly*, xii., No. 4.

sistency with which it takes up and retains impurities derived from the solution.

Cond.—No bases other than fixed alkalies should be present.

Sol.—Dissolved readily by mineral acids. Soluble or prevented from precipitation by NH_4 salts and tartrates, citrates, &c , or other organic solutions,

Contam.—Alkali used as the precipitant, Fe_2O_3, Al_2O_3, and silica from the reagents. The precipitate requires thorough washing by decantation with boiling water. After ignition and weighing, it should be dissolved in HCl, which leaves SiO_2 and Al_2O_3. From this solution the iron should be precipitated by ammonia, filtered, re-dissolved, and re-precipitated again, and these impurities ignited, weighed, and the weight deducted.

Ign.—If only moderately, some Ni_2O_3 is contained in the precipitate. If strongly ignited, it all becomes *green* NiO. The tint is not a pure green like that of ignited Cr_2O_3, but lighter and somewhat muddy.

$NiS.H_2O$.

Rem.—For separation only. Usual precipitant H_2S in weak acetic solution, or $(NH_4)_2S$ followed by acetic acid in excess. Oxidises easily in contact with the air, with partial formation of $NiSO_4$. Should be washed by and kept in contact with H_2S water during manipulation.

Cond.—Absence of other members of $(NH_4)_2S$ or H_2S group. NH_4Cl in the solution assists materially its separation in the granular form. Free ammonia, on the other hand, tends to keep the precipitate suspended in the liquid. The solution should be only slightly acid with acetic acid or else barely alkaline.

Sol. — Formation of the precipitate prevented by moderate amounts of free acetic acid or mineral acids. When once formed, it is insoluble in these menstrua unless oxidised by exposure to air, which may easily occur. Somewhat soluble in $(NH_4)_2S$. To meet these peculiarities of the compound, the solution should be rendered alkaline with ammonia, and H_2S passed in, or $(NH_4)_2S$ added, and when the precipitate is *fully formed*, the solution is acidified with acetic acid, and the precipitate allowed to settle (which occurs readily if NH_4Cl is present). Soluble in hot HNO_3 or in aqua regia. Soluble in KCy.

Contam.—Sulphides of $(NH_4)_2S$ group, if not previously separated.

Ign.—Gives mixture of oxide and sulphate.

$Co_2 (NO_2)_6 6KNO_2$.

Rem.—Usual precipitant, KNO_2 in a solution slightly acid with acetic. Yellow crystalline precipitate, forming best in a warm solution.

Cond.—Solution should contain only Co, Ni, and K salts. It should be a nearly saturated solution of $KC_2H_3O_2$, containing but little free acetic acid.

Sol.—Dissolved by H_2O, acids, NH_4 salts, NaCl, and most other Na salts. Insoluble in $KC_2H_3O_2$ and other K salts. Insoluble in dilute acetic, and in alcohol. The precipitate should be first washed with a 10 per cent solution of $KC_2H_3O_2$, and the latter salt finally removed by washing with alcohol.

Contam.—If Ca or other alkaline earths are present, a yellow NiCa nitrite, similar in properties (solubility, &c.) to the Co compound will separate. Pb also gives a similar compound. Care in washing off K salts is necessary.

Ign.—By addition of H_2SO_4 and ignition, the precipitate is converted to $3K_2SO_4+2CoSO_4$. One method of management consists in dissolving the washed precipitate through the filter with a little hot dilute H_2SO_4 into a weighed capsule, evaporating, and igniting. Some $KHSO_4$ may remain after ignition; removed by addition of a small lump of solid ammonium carbonate and igniting.

$CoS.H_2O$.

Rem.—For separation only. Properties essentially the same as those of $NiS.H_2O$. Precipitant, H_2S in weak acetic solution or $(NH_4)_2S$. Oxidises readily in the air when moist, some sulphate being formed. Should be kept in contact with H_2S water during filtration.

Cond.—Absence of other members of $(NH_4)_2S$ or H_2S group. NH_4Cl assists the separation. Unlike $NiS.H_2O$, free NH_4OH does not materially influence the separation. Solution should be preferably *slightly* acid with acetic before filtration (vide $NiS.H_2O$).

Sol. — Formation of the precipitate prevented by moderate amounts of free acetic or mineral acids. When once formed, however, it is insoluble in these menstrua. Of the ordinary mineral acids, HCl has the strongest preventive effect, H_2SO_4 the least; but a very small amount of free H_2SO_4 retards the separation markedly. Soluble in hot HNO_3 or in aqua regia; also in KCy.

Contam. — Usually accompanied by Ni or other members of the group if not previously separated.

Ign.—Affords mixture of oxide (Co_3O_4) and sulphate.

Cu.

Rem.—Obtained by electrolytic deposition on platinum from acid solution. Free HNO_3 gives a bright coating. Too strong a current gives a spongy imperfectly adherent coat.

Cond.—Sulphuric acid solution preferable, with or without a few drops of nitric acid. Not over 8 per cent of free acid should be present. Chlorides disadvantageous. Organic acids (as citric, &c.) should not be present, since they afford a brittle deposit containing organic elements.

Sol.—Easily soluble in HNO_3. When that acid is present at the end of the operation, flood out the dish with water before breaking the current. Deposit dissolved or prevented from forming by Cl, lower oxides of nitrogen, or too strong acid.

Contam.—If free HNO_3 is absent, As, Sb, or Bi may occur in the deposit, rendering it blackish. A black colouration is, however, sometimes due to other causes. If free HNO_3 is present, Zn, if present, begins to deposit (imperfectly) as soon as all the Cu is precipitated. Pb and Mn may separate from the solution on the other pole, as PbO_2 or MnO_2, and in case a dish is used these oxides may fall to the bottom and be caught in the deposit. $SnO_2(xH_2O)$ may also separate from the solution and be caught in the deposit in the same way.

Ign.—Easily oxidised by heating in air or oxygen. After deposition and washing with water, the water should be rinsed off with alcohol, the alcohol drained off, and the dish dried at a temperature which can be borne by the hand, not higher.

CuO or $3CuO.H_2O$.

Rem.—Usual precipitant, KOH or NaOH in a boiling solution or one subsequently boiled. Na_2CO_3 or K_2CO_3 may also be used in the same manner. The precipitate, at first the light bluish hydrate or basic carbonate, becomes black on boiling from elimination of H_2O.

Cond.— Alkaline solution, not containing bases, the hydrates of which are more or less insoluble. NH_4 salt and organic substances should be absent.

Sol.—Dissolved by acids, also by NH_4 salts and organic solutions, as citrates, &c. Precipitation prevented by alkaline bicarbonates, especially by $KHCO_3$.

Contam.—Chiefly the alkali of the precipitant, which is washed out with great difficulty. Some SiO_2 dissolved by the reagent from the bottle in which it was kept, or otherwise introduced, may also be present. Left behind on dissolving in acid the ignited and weighed precipitate.

Ign.—Obtained as black CuO. Some reduction to the metallic form by contact of C may occur, but as the metal is not volatile it is readily restored by ignition with a few drops of HNO_3. The use of platinum where reducing substances may be mingled with the precipitate is inexpedient. Precipitate quite hygroscopic after ignition.

CuS.

Rem.—Usually for separation. When for determination, treated as suggested under "*Ign.*" for production of

Cu$_2$S. Has ordinarily a brown to black colour, but when precipitated along with sulphur has an orange-red colour.

Cond.—Acid solution usually used, though not indispensable. Precipitation can be effected promptly in presence of moderately strong H$_2$SO$_4$, or of HCl if not too strong or hot. If HNO$_3$ is present, the solution must be dilute and cold.

Sol.—Soluble in hot dilute HNO$_3$ and in HCl when hot and moderately strong. Somewhat soluble in (NH$_4$)$_2$S, especially if polysulphides are present. Insoluble in HCl or H$_2$SO$_4$, or in NaHS, or KHS, unless polysulphides are present.

Ign.—Partly reduced to Cu with C. Converted to Cu$_2$S by mixing with sulphur and igniting in a current of hydrogen (in a Rose crucible).

PbSO$_4$.

Rem.—Usual precipitant, H$_2$SO$_4$. By digestion with alkaline carbonates or bicarbonates, it is converted to PbCo$_3$.

Cond.—Solution should be acid with H$_2$SO$_4$, and contain little or no free HNO$_3$ or HCl. The larger the proportion of these acids and the warmer the solution, the more H$_2$SO$_4$ required. NH$_4$ salts and salts of organic acids should not be present. Also, any large proportion of chlorides.

Sol.— Readily soluble in concentrated mineral acids, H$_2$SO$_4$, as well as the others, but less soluble in dilute H$_2$SO$_4$ than in pure water. Soluble in Na$_2$S$_2$O$_3$, in caustic alkaline solutions, and in ammonia salts, notably those of organic acids, especially when free ammonia is present. NH$_4$C$_2$H$_3$O$_2$ and (NH$_4$)$_3$C$_6$H$_5$O$_7$ may be used for this purpose. To obtain PbSO$_4$ for ignition and weighing, the usual procedure is to wash off all other substances with very dilute H$_2$SO$_4$, and then to remove the latter before drying by washing with alcohol.

Contam.—If all other sulphates (than PbSO$_4$) have not been removed by washing with dilute H$_2$SO$_4$ as just described, the precipitate may be contaminated with sulphates, most of which are insoluble in alcohol.

Ign.—Unchanged by a moderate heat. At temperatures usually higher than are ordinarily obtained with a Bunsen burner, the compound may fuse, but without volatilisation.

With C partially or entirely reduced to Pb, PbS, &c., which are volatile. The precipitate should be separated from the filter paper, which should be separately incinerated (in the cover of the *porcelain* crucible) with the aid of a few drops of concentrated HNO$_3$ and H$_2$SO$_4$, the ashes and the precipitate united and the whole ignited before weighing.

(To be continued).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.
November 6th, 1891.

Dr. E. ATKINSON, Vice-President, in the Chair.

MISS ALICE LEE, Mr. W. A. Shenstone, and Mr. Frank McLean were elected Members.

Prof. SYDNEY YOUNG, D.Sc., read a paper on "*The Generalisations of Van der Waals Regarding 'Corresponding' Temperatures, Pressures, and Volumes*," in which he gave the results of an investigation made with a view of testing whether these theoretical deductions agree with experimental facts.

From his virial equation—

$$\left(p + \frac{a}{v^2} \right) (v - b) = R (1 + a t),$$

Van der Waals showed that if the absolute temperatures of various substances be proportional to their absolute critical temperatures, their vapour pressures will be proportional to their critical pressures, and their volumes, both as liquid and as saturated vapour, will be proportional to their critical volumes. These deductions have now been put to the test of experiment.

Some years ago Prof. Ramsay and the author published data relating to the temperatures, pressures, and specific volumes of methyl, ethyl, and propyl alcohols, ether, and acetic acid. Since then, experiments have been made on benzene and its halogen derivatives, fluor-, chloro-, bromo-, and iodo-benzene, carbon tetrachloride and stannic chloride, and in a few cases the observations have been carried to the critical points.

The critical volumes being in many cases difficult to determine with any exactness, the author, instead of expressing the temperatures, pressures, and volumes of each substance in terms of their critical values, found it necessary to compare the various substances with one of them taken as a standard. Fluor-benzene was chosen as standard on account of the very simple relations observed between the mono-halogen derivatives of benzene, and the fact of its critical constants (temperature, pressure, and volume) having been determined with considerable accuracy.

Some of the critical constants of the various substances examined are given in the accompanying table, the brackets indicating calculated values.

Other tables of experimental data,—including boiling-points at corresponding pressures, vapour pressures at corresponding temperatures, molecular volumes of liquid, and saturated vapours at corresponding pressures and at corresponding temperatures,—and ratios calculated therefrom, accompany the paper. From these the author infers (1) that Van der Waal's generalisations are nearly true for chloro-, bromo-, and iodo-benzene, when compared with fluorbenzene; (2) that for benzene, carbon tetrachloride, stannic chloride and ether, the generalisations may only be taken as rough approximations to the truth, and (3) that for the three alcohols and acetic acid they do not hold good at all. The tables further show that more consistent results are obtained when the comparisons are made at corresponding pressures rather than at corresponding temperatures, particularly in the case of molecular volumes of saturated vapours.

The subject of saturated vapours is also treated by another method. If Van der Waal's deductions were strictly true, then the ratios of the actual densities of the saturated vapours of different substances to their theoretical densities should be equal at corresponding pressures. These ratios have therefore been calculated, and show an approximate agreement amongst benzene and its halogen derivatives, carbon tetrachloride, stannic chloride, and ether. For the other substances the agreement is less satisfactory. It is also noted that the ratio of the actual critical density to the theoretical density is for many substances about 4·4.

The alcohols differing so widely from the other compounds were compared amongst themselves instead of with fluorbenzene, with the result that somewhat closer agreement was found, but the deviations were still far outside the limits of experimental error.

Of the critical constants the volumes are the most difficult to determine, because at the critical point the curves connecting temperature and volume, and pressure and volume, are parallel to the axes of volume. Accordingly, the author in some cases has deduced this quantity by plotting against temperature, the numbers representing the ratios of the molecular volumes both of liquid and saturated vapour to those of fluorbenzene at corresponding temperatures and also at corresponding pressures. Four curves result which should intersect at the critical temperatures, and the point of intersection gives the ratio of the molecular critical volume of the substance to that

Substance.	Formula.	Temperatures. ° C.	Pressures in vapour of mercury.	Volumes in C.c.	
				Of a grm.	Molecular.
Fluorbenzene	C_6H_5F.	286·55	33,912	2·43	233
Chlorobenzene	C_6H_5Cl.	(360)	(33,912)	2·34	(262)
Bromobenzene	C_6H_5Br.	(397)	(33,912)	1·76	(275)
Iodobenzene	C_6H_5I.	(448)	(33,912)	1·47	(298)
Benzene	C_6H_6.	288·5	36,395	2·82	219
Carbon tetrachloride	CCl_4.	283·15	34,180		
Stannic chloride	$SnCl_4$	318·7	28,080		
Ether	$(C_2H_5)_2O$.	194·4	27,060		
Methyl alcohol	CH_3OH	240·0	59,760		
Ethyl	C_2H_5OH.	243·1	47,850		
Propyl	C_3H_7OH.	263·7	38,120		
Acetic acid	$CH_3.CO.OH$.	321·6	43,400	2·46	147

of benzene. This method leads to results in fair accord with direct determinations.

In the discussion which followed the reading of the paper, Prof. RAMSAY said the results proved that Van der Waal's generalisations were only rough approximations, and he suggested that some force had been neglected, or a term omitted from the equations. Perhaps the assumption that the molecules are incompressible was not correct. He also strongly protested against the tacit assumption of the Van der Waal's laws, and deductions made therefrom, which had recently become so common, particularly in German text-books.

Prof. PERRY inquired whether the quantities *a*, *b*, and *a* had been determined for different substances and found to be constant.

Prof. RAMSAY said that for substances in states analogous to those of perfect gases the quantities were approximately constant, but when the liquid state was approached this was no longer true. According to Prof. Tait the two states were not continuous.

Prof. HERSCHEL remarked that Prof. Tait had established his law on the assumption that the co-volume is four times the volume occupied by the molecules. This law, he said, had been amply verified by experiments on explosions.

Dr. BURTON, referring to Prof. Ramsay's remarks on the compressibility of molecules, said the law of force between attracting molecules should be accurately known before any deductions were made; and he pointed out that at constant volume the pressure should be proportional to the absolute temperature if allowance be made for the negative pressure of attraction.

Mr. BLAKESLEY, in speaking of molecular forces, said he had observed that when water is allowed to evaporate from glass, a furrow is formed in the glass which marks out the original boundary of the liquid. To all appearances the particles of glass are torn away by the molecular forces acting along the boundary.

NOTICES OF BOOKS.

Solutions. By W. OSTWALD, Professor of Chemistry in the University of Leipzig. Being the Fourth Book, with some Additions, of the Second Edition of Ostwald's " Lehrbuch der Allgemeinen Chemie." Translated by M. M. PATTISON MUIR, Fellow of Gonville and Caius College, Cambridge. London: Longmans, Green, and Co. 8vo., pp. 316.

IN the Translator's notice we are informed that a systematic arrangement of the facts concerning solutions already established and a formal statement of the theory are to be found only in Prof. Ostwald's work. The theory of solution is, indeed, of very recent origin, and is chiefly due to the researches of van 't Hoff. Prof. Ostwald considers in succession solutions in gases, solutions of gases in liquids, solutions of liquids in liquids, and solutions of

solids in liquids. He next takes up osmose, diffusion, the vapour pressures of solutions, their freezing-points, salt solutions, and the simultaneous action of several solvents.

The importance of a study of the laws of solution is fully shown in the author's concluding remarks. The laws of solution, he considers, resemble the laws of gases discovered towards the end of the last century, the one and the other being colligative in character. But the region included under solutions is far wider than that dealt with under gases. Innumerable substances are not met with in the gaseous state, whilst few indeed cannot be brought into solution, the silicates being the chief exceptions. Almost all the chemical processes occurring in Nature, in organisms as well as in the inorganic crust of the earth, are carried out between substances in solution. Hence the attention which chemists have recently paid to the phenomena and the laws of solution is not merely justifiable, but is necessitated by the present position of chemical science and its future prospects. There is no other work in the language in which this subject is discussed as ably and as fully.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxiii., No. 18, November 2, 1891.

Memoir by M. Armand Gautier accompanying the Presentation of his Work on Biological Chemistry.—The work is divided into five parts, in which the author expounds in succession the origin of the proximate principles and the mechanisms which give rise to them in plants and animals; the especial history of each of the chemical species which enter into the structure of organised beings; the composition of the tissues, humours, and secretions; the general functions which insure the life of each individual, and lastly, the mechanism of the general life, the sources which maintain the activity and the functionation of animals, and the relations established in them between the consumption of food and the transformation of its latent energy into heat, mechanical work, and growth. The author showed in 1877 that the green substances of plants hitherto confounded under the name of chlorophyll differ respectively among the dicotyledons, the monacotyledons, and the acotyledons. They even seem according to some analyses to vary in the different species of each class. He has given a method for preparing these substances in a pure crystalline state, and has shown that the chlorophylls produce by reduction a derivative which he called *colourless chlorophyll*, and which has since been known as protophylline. Reduced chlorophyll plays a very important part in the syntheses

effected in the leaf. The author expounds in his work his views on the constitution of uric acid and of the bodies of the uric and xanthic series. The number of the known xanthic bodies has been increased from three (xanthine, sarcine, and guanine) to at least twelve. He has refuted the erroneous opinion that plants alone were capable of furnishing alkaloids, and shown, on the contrary, that in every animal cell which acts normally alkaloids are necessarily formed. He has also undertaken the study of the albumotoxines, which he considers intermediate between the ordinary albumenoids and the alkaloids properly so-called. In a different order of ideas he has shown that psychic work, the phenomena of consciousness, thought, and will, are not correlated with any expenditure of energy, mechanical, chemical, or thermic, but enter into a class of facts prepared solely by the physico-chemical acts, of which the nerve centres are the seat, but which are not commensurable with psychic acts.

Researches on the Monobromobutylenes. — E. Reboul.—The object of this memoir is to make known a new bromobutylene formed by eliminating HBr from ethylethylenebromide. Its structure is represented by the formula $CH_3 - CH_2 - CBr = CH_2$. It is a colourless liquid of an odour like garlic, and of the specific gravity 1·282 at $+21°$. It boils at 88° under a pressure of 0·759 metre.

The Direct Combination of Metals with Chlorine and Bromine.—Henri Gautier and G. Charpy.—Most metals, except aluminium, are scarcely attacked by dry chlorine and bromine at the ordinary temperature. It is very remarkable to see magnesium completely resisting the action of those liquids which attack aluminium. But if the action of the dry halogens is slow it becomes rapid in presence of water.

Contribution to the Physico-Chemical Study of the Function of the Kidneys.—C. Chabrié.—The first operation of the kidneys is a filtration analogous to that employed in the laboratory to separate a fine precipitate from the supernatant liquid. Secondly, the kidney acts as a dialyser. Urea, which has a small molecular volume, traverses the porous septa more rapidly than albumen, the volume of which is considerable.

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Journal fur Praktische Chemie.
New Series, Vol. xliii., Part 12.

The Formation of Sorbose.—A. Freund.—Sorbose is formed by the oxidation of a gelatinous substance contained in the berries of the service-tree.

Researches from the Laboratory of the University of Freiburg.—Ad. Claus.—These researches consist of a paper on absolute localisations by the transfer of paradinitro compounds into quinones.

Researches on Alloisomerism. — A. Michael and O. Schulthess.—A dissertation on the elimination of halogens in α-β-ethers of haloid acids. The authors examine the action of zinc upon α-β-dibrompropionic ethers, upon α-β-dibrombutyric ethers, dibromsuccinic ethers, citra and itadibrompyruvic ethers, also upon α_2-β-trichlorbutyric ethyl ether.

Small Contributions from the Laboratory of E. von Meyer.—These comprise a paper by L. Harting on hexamethyleneamine, and one on acetone potassa and acetone soda by W. Vaubel.

New Series, Vol. xliv., Nos. 13 and 14.

Researches from the Organic Chemical Laboratory of the Technical High School at Dresden.—Communicated by Prof. R. Schmidt.—These researches include papers by R. Schmidt and H. Hähle on pyrocatechin carbonic acids, by H. Hähle on a new method of preparing phenoldicarbonic acids, and by P. Otto on the action of chlorocarbonmonoxide upon glycolchlorhydrines.

Bismuth of Commerce and Purified Bismuth along with Remarks on the Atomic Weight of this Metal.—R. Schneider.—A controversial paper with reference to the recent memoir by Prof. Classen on the atomic weight of bismuth (*Journal*, xliii., 133). It does not admit of abstraction.

Contributions to the Chemistry of the Rhodium-Ammonium Compounds.—S. M. Jörgensen.—These include papers on the luteochodium salts, and on acid luteo- and roseo-nitrates.

Researches from the Laboratory of the University of Freiburg.—These consist of papers by C. Willgerodt and L. Ellon on the nitrohaloid-, hydrazo-, and nitrosohaloidazo-compounds; by Ad. Claus and W. Neukrantz on the oxidation of the mixed fatty aromatic ketones by potassium permanganate potassa, and by Ad. Claus and R. Wehr on paratolyl acetic acid.

Communications from the Chemical Institute of the University of Kiel.—These comprise a memoir by Th. Curtius on the nomenclature of organic compounds which contain two atoms of nitrogen in mutual combination. The author proposes that two atoms of nitrogen in simple combination, representing the quadrivalent radicle $\left(\begin{array}{c} N \\ | \\ N \end{array}\right)^{IIII}$, form the azi-group, to be written azine at the end of a word. Two double combined atoms of nitrogen representing the bivalent radicle $\left(\begin{array}{c} N \\ || \\ N \end{array}\right)^{II}$, form the well-known azo-group, which at the end of a word is written azone. As soon as one of these radicles is partially or entirely saturated with hydrogen the syllable "hydr" is prefixed to "azi" and "azo." Thus we have the names "hydrazo" and "hydrazi," becoming at the end of a word "hydrazone" or "hydrazine." All possible bodies with two mutually combined atoms of nitrogen, such as the azo-, diazo-, and hydrazine compound, are derived from hydrazone (diimide, a body not yet obtained), or from hydrazine (diamide) by the substitution of hydrogen. Prof. Curtius also communicates a memoir on diammoniumsemisulphate.

Oxyderivatives of Alizarin Blue.—R. E. Schmidt and L. Gattermann. — The substances obtained are dioxyalizarin blue, formed by the action of fuming sulphuric acid of a very high percentage upon anthraquinone. Its composition is $C_{17}H_7NO_4.(OH)_2$. It is almost insoluble in ordinary solvents. In concentrated sulphuric acid it dissolves with a bright greenish blue colour, and the solution when examined with the spectroscope shows two sharp absorption bands in the red and the orange. The vapour of this compound has a rich violet colour like that of iodine. Trioxyalizarin blue, $C_{17}H_6NO_4.(OH_3)$, agrees in its spectrum with that of the quinoline derivative of alizarin bordeaux.

Transformation of Bibrom-succinic Ester with Zinc.—Ad. Claus.—A controversial paper not admitting of useful abridgment.

New Series, Vol. xliv., No. 15.

Lævulinic Acid and Acetondiacetic-dilacton.—Arthur Michael.—The author institutes a comparison between levulinic ethylethers obtained by different methods. He examines its behaviour with phenylhydrazine-hydrochlorate, with hydroxylamine, and the behaviour of acetondiacetic-dilacton with hydroxylamine and phenylhydrazin-hydrochlorate.

Appendix to Pyridinebetaine.—Dr. Krüger.—The author refers to his memoir on the pyridine bases, in which he mentioned that pyridinebetaine on treatment with sodium amalgam passes into a body which, in an alkaline solution, takes an intense blue colour if heated. The double bases formed by the addition products of

pyridine with methylethyl- and amyl-iodides display this blue colouration with remarkable intensity. The general result of the author's experiments is that all the pyridonium compounds formed by the addition of pyridine to halogenous substituted bodies of the fatty series, on reduction with sodium amalgam, zinc-powder, or a mixture of zinc and iron powder, in aqueous or alcoholic solution, yield a blue colour. This coloured reaction is a convenient means of ascertaining whether a body under examination can be a pyridonium compound or not.

Ring and Nucleus Formation of the Carbon Compounds.—W. Vaubel.—This memoir cannot be usefully reproduced without the accompanying diagrams.

Constitution of Cymol.—M. Filetti.—The author's experiments confirm fully the assertions of Widman ; cymol does not contain normal propyl, but is an isopropyl derivative. The assumed transformations of the propyl group in the cuminic and cymol series is thus deprived of all foundation.

The Degree of Concentration of Solutions as Determined by their Refractive Power.—H. O. G. Ellinger.—The author considers the oleorefractometer of Amagat and Jean as especially adapted for such determinations, but thinks "differential refractometer" a more suitable name. His results are given in a tabular form.

Optical Analysis of Butter Fat.—H. O. G. Ellinger. —If natural butter, which gives the highest value (35°) is mixed with equal parts of margarine, the reading obtained is 21¼°, that is, it falls below the lowest figure of natural butter (23°). The optical method thus fully detects a sophistication with any quantity of margarine not less than 45 per cent.

On Polymeric Trichloracetonitril.—N. Tscherwen-Iwanoff.—The polymerisation is effected by the prolonged action of dry hydrochloric acid and exposure to light.

Revue Universelle des Mines et de la Metallurgie.
Series 5, Vol. xv., No. 1.

Application of the Basic Process to Refining Copper.—Percy E. Gilchrist.—From the *Journal of the Society of Chemical Industry.*

No. 2.

Detection and Determination of Aluminium in Cast Irons and Steels.—A. Carnot.—Taken from the *Comptes Rendus*, and already noticed.

Determination of Silica in Presence of Iron.—M. Leclerc.—Already noticed under the *Comptes Rendus*, from which it is taken.

MISCELLANEOUS.

The Crystal Palace Electrical Exhibition.—A meeting of the Honorary Council of Advice, and of the Special Committee appointed by the Electrical Section of the London Chamber of Commerce, will, by kind permission of the Lord Mayor, be held at the Mansion House at 3 o'clock on Wednesday, the 25th inst., when a report on the progress of the Exhibition will be presented, and the question of how the Exhibition may best be used as a means of advancing the interests of electrical science will be considered. The Lord Mayor will preside. The whole of the space is now practically allotted, extra buildings having been erected for certain large installations which could not otherwise have been accommodated.

Optical Determination of the Quantity of Albumen in Urine.—H. O. G. Ellinger.—By means of the oleorefractometer of Amagat and Jean (differential refractometer) the author has determined the quantities of albumen in urine with approximate accuracy.—*Journ. fur Prakt. Chemie.*

THE CHEMICAL NEWS.

VOL. LXIV., No. 1670.

STUDIES ON SAPONIFICATION.
No. I.

By ALFRED H. ALLEN.

In a recent number of the CHEMICAL NEWS (vol. lxiv., p. 201), Mr. J. A. Wanklyn took strong exception to my statement (p. 179) that Messrs. Wanklyn and Fox had never published a single original experiment in support of their assertion that the proportion of glycerin yielded by the saponification of butter and other fats exhibits any grave departure from the amount required by the accepted view of their constitution. Mr. Wanklyn pointed out a fact of which I was fully aware, but had omitted to mention through inadvertence, namely, that in January last he read a paper before the London Section of the Society of Chemical Industry, in which he described an experiment which he considered proved that butter yielded only 6·2 per cent of glycerin on saponification, instead of the 11 or 12 per cent which is required by the ordinary theory and which agrees with the determinations of various observers.

Mr. Wanklyn lays much stress on his experiment—the only one of the kind he has published—as affording proof of his ingenious but otherwise unsupported isoglyceride theory, which I fully described in a paper recently published in these columns (p. 179).

As Mr. Wanklyn complains of his experiment having been left unnoticed by me, and believes that chemists will find great difficulty in resisting the conclusion which follows from the experiment, I propose to submit it to a critical examination, and to show that Mr. Wanklyn's

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50 grms. of butter-fat was mixed with 9·42 grms. of dry slaked lime, and the mixture heated in an open dish at 100° C. for a long time and constantly stirred. 6·46 grms. more slaked lime was then added, the mixture treated with boiling water, and the liquid filtered.

Aqueous extract was neutral in reaction. Evaporated it left *residue* weighing—	*Residue.*—Treated with boiling alcohol and liquid filtered.	
	Alcoholic Extract.—Evaporated, left *residue* weighing 4·606 grms. This when treated with water and the liquid filtered gave—	*Residue*, consisting of insoluble lime salts, &c., was apparently not further examined.
	Solution, evaporated, gave resid. weighing—	*Residue* (by difference) weighed—
1·991 grm.	1·405 grm.	3·201 grm.
These two residues together contained 0·300 of *lime*, determined, leaving— 3·096 grms. of "glycerin."	Said to contain no unchanged butter. Apparently not further examined.	

published account of it (*Journ. Soc. Chem. Ind.*, x., 89) contains abundant internal evidence of its inconclusive nature.

Mr. Wanklyn's experiment was based on the saponification of butter-fat with slaked lime; the solution of the resultant glycerin from the product by water and alcohol, evaporation of these solutions, and weighing of the residues. In one or two respects Mr. Wanklyn's mode of procedure is implied rather than actually expressed, but the accompanying table represents what I understand him to have done, and I believe is an accurate statement of the facts.

The foregoing is a synopsis of Mr. Wanklyn's procedure and results, but it is necessary to describe them more fully, and in doing this I shall, whenever possible, make use of Mr. Wanklyn's exact works.

To commence with, I may say that Mr. Wanklyn stated that the butter he employed came direct from one of the best London dairies, and that he quite appreciated the necessity of making sure of the genuineness of the material. It may therefore fairly be assumed to have been of normal character.

In making his experiment Mr. Wanklyn "took 50 grms. of butter with 9·42 grms. of dry hydrate of lime, making a total of 59·42 grms. These materials were placed in a platinum dish provided with a stirrer, and the vessel with its contents was heated on the water-bath and constantly stirred for a long period. From time to time it was allowed to cool, and was then weighed, five times in all. There was a steady loss of weight, and ultimately the weight of the compound fell to 58·510 grms., showing a loss of 0·910 grm. of water."

Mr. Wanklyn then points out that "hydrate of lime and a glyceride react without production of water, yielding only lime salts and glycerin. The loss of water could arise from two sources; either from the action of free fatty acid in the butter, or from the action of lime on an isoglyceride." Mr. Wanklyn states that "possibly there is a third way" in which water might be formed, but does not say what it is. I suggest the well-known reaction $CaH_2O_2 + CO_2 = CaCO_3 + H_2O$.

Mr. Wanklyn makes the bold assumption that no loss of glycerin will occur when a mixture of glycerin, slaked lime, and fatty acid salts of lime is heated for a long period to 100° C. in an open dish with constant stirring. This is so opposed to the known behaviour of glycerin under somewhat similar conditions that it should have been *proved*, and not simply *assumed*, to be the fact. If glycerin volatilised during the first stage of Mr. Wanklyn's experiment, the whole value of the operation, which was to prove deficient production of glycerin, is nullified. As a matter of fact Mr. Wanklyn observed a loss of 0·910 grm., which he assumed, but did not prove, to have been due to the evaporation of water formed by one of the reactions indicated.

Throughout his paper Mr. Wanklyn does not appear to contemplate the possibility of the absorption of atmospheric carbonic acid by slaked lime exposed to the air and constantly stirred. If this occurred, and glycerin as well as water volatilised, the actual loss of glycerin was considerably in excess of the loss of weight observed.

Mr. Wanklyn then added to his product a further quantity of 6·46 grms. of hydrate of lime, although the amount previously used was more than equivalent to the fatty acids of the butter. Why the second addition was made is not stated and is not apparent, nor does Mr. Wanklyn state whether he continued the operation of heating and stirring the mixture after adding the further quantity of lime. My impression is that he did.

Mr. Wanklyn next digested the mixture with 600 c.c. of water, using the solvent boiling and in successive portions. The undissolved portion was treated with 300 c.c. of boiling alcohol, which was evaporated in its turn; the residue obtained being weighed and then apparently treated with water, and the filtered liquid again evaporated. How much glycerin was lost by evaporation

during the latter stages of the process of concentrating the aqueous and alcoholic liquids is of course unknown. That dilute solutions of glycerin can be concentrated to a considerable extent without loss is admitted, but the accepted view that glycerin volatilises from its concentrated solutions at 100°, and is itself volatile at that temperature, is based on too many observations to be ignored or pooh-poohed, unless rigid experimental demonstration be afforded showing that previous observers have been in error. This proof Mr. Wanklyn does not furnish.

The following are Mr. Wanklyn's results :—

	From 50 grms. of Butter.		= per cent.	
Aqueous residue	1·991	} 3·396	3·982	} 6·792
Alcoholic residue { Soluble	1·405		2·810	
{ Insoluble	3·201		6·402	
Insoluble lime salts	58·140			
	64·737			
The material that produced them..	64·970			

Mr. Wanklyn points out that the agreement between the weight of the materials taken and the products was very close, showing that "nothing important had escaped by evaporation or was otherwise lost."

Mr. Wanklyn states that the aqueous extract was not alkaline, which "shows that the whole of the hydrate of lime was used up, and that perfect action must have taken place; and for every equivalent of butter acids there were two equivalents of lime." As a matter of fact the proportion of lime used was sensibly in excess of two equivalents; twice the quantity requisite to effect the saponification of 50 grms. of average butter being 14·98 grms., whereas Mr. Wanklyn employed 15·88 grms. Mr. Wanklyn gives no clue to what used up the second equivalent, to say nothing of the excess of lime. Perhaps it combined with atmospheric carbonic acid, absorbed while the mixture was being heated, with constant stirring, in an open dish on the water-bath for a long period; but if so, what becomes of the argument from the approximate concordance between the weight taken and that of the product obtained? If carbonic acid was gained, something—perhaps glycerin—was lost in addition to the displaced water of the slaked lime, or the weight would have increased instead of somewhat diminishing. The fact that the aqueous solution of the product was not alkaline, although excess of lime was used, goes rather to prove extensive absorption of carbonic acid, and the care with which Mr. Wanklyn stirred, than that all the lime (second equivalent and excess) had reacted with the butter.

Mr. Wanklyn regards the difference between the weight of the material taken and the products obtained (amounting to 0·233 grm.) as having been due to the formation and volatilisation of butyric ether. But if saponification was complete, and the exhaustion of the product with water was perfect, all butyric acid must have been dissolved as calcium butyrate. How, then, can Mr. Wanklyn account for the formation of butyric ether? It could not have been formed during the treatment with water, for there was then no alcohol present; and it could not have been formed in the alcoholic treatment, for all butyrate must have been previously dissolved by the water.

This brings us to the next anomaly. Thousands of analyses by scores of observers have proved that butter yields on saponification about 5½ per cent of butyric acid. Whether the source of that acid be a glyceride or iso-glyceride is immaterial. Now 5·5 per cent of butyric acid corresponds to 6·688 of butyrate of calcium, which is a salt soluble both in water and alcohol. It is more soluble in cold water than in hot, but readily in either, and should certainly have been dissolved out by the repeated treatments with water and alcohol to which Mr. Wanklyn subjected his product of saponification. But

Mr. Wanklyn's soluble extract only amounted to 6·792 per cent, so that if he dissolved out all his butyrate of calcium he only obtained 0·104 of glycerin, instead of 6·2 per cent, which he admits and claims to have obtained. But that Mr. Wanklyn did *not* dissolve out all the calcium butyrate which must have resulted from complete saponification is evident from the amount of lime in his soluble extracts, which he "determined in each case by actual experiment," and found to be "*about* 3 decigrammes."

Now 0·300 of lime represents 1·146 grms., or 2·292 per cent, of calcium butyrate, which is the amount Mr. Wanklyn apparently obtained in solution, against 6·688 per cent which he ought to have obtained. But it is curious that Mr. Wanklyn did not calculate the lime he found in his extracts to calcium butyrate, and deduct *this* from the weight of the residues in order to deduce the glycerin; especially as he had observed that the aqueous extract was not alkaline in reaction, and therefore that the lime existed as a neutral salt. It is an astounding fact that throughout the description of his experiment Mr. Wanklyn completely ignores the formation of butyrate of calcium! His results might have been yielded by tallow instead of butter, for all the figures show to the contrary. I imagine that only on the ground that butter yields an insignificant proportion of butyric acid on saponification can Mr. Wanklyn justify his omission to calculate his lime to butyrate before deducing the weight of glycerin from his result. Mr. Wanklyn did at one time hold this heterodox view, although other chemists were daily obtaining results showing the formation of 5 to 6 per cent of butyric acid; but Mr. Wanklyn now himself admits the errors of his former views, and has formulated his iso-glyceride theory to account for the accepted fact of the production of butyric acid in considerable proportion.

Assuming Mr. Wanklyn to have succeeded in effecting complete saponification, he is on the horns of a dilemma. (*a.*) If his calcium butyrate was wholly dissolved, then his lime determinations were wrong; and there was only an insignificant quantity of butyric acid produced. (*b.*) If his lime determinations were correct, he only dissolved out about one-third of the total calcium butyrate; and if he failed to dissolve the remainder, what guarantee is there that he was any more successful in extracting the glycerin? The only way out I can imagine for Mr. Wanklyn would be for him to suppose the formation of a basic butyrate of calcium by the action of the second equivalent of lime, and the insolubility of this hypothetical compound both in boiling water and in alcohol. A salt having such properties would be very valuable to those desiring to determine butyric acid. But even this resource appears to fail; for I have added to butyric acid prepared from butter twice the quantity of lime-water requisite to convert it into the neutral butyrate of calcium, evaporated the liquid to dryness, and taken up the residue with water. The insoluble portion effervesced strongly with dilute sulphuric acid, and, when the filtered liquid was distilled, the distillate contained only a mere trace of butyric or other volatile acid.

Correcting the amount of soluble extract (=6·792 per cent) obtained by Mr. Wanklyn by the calcium butyrate (2·292 per cent), corresponding to the lime determined in the extract, there is only 4·500 per cent of glycerin obtained in the experiment, or a little more than one-third of the amount which should have been found if butter possessed the character of an ordinary glyceride. But Mr. Wanklyn only obtained a little more than one-third of the proper amount of butyrate of calcium, so that it really seems probable that he only succeeded in saponifying something like one-third of the butter employed. This suggestion explains the results from one point of view, but Mr. Wanklyn urges that saponification must have been complete, (1) because all the lime had been used up, and (2) because boiling alcohol did not dissolve out of the product any unchanged butter. The first of these observations I have already shown is no

proof of complete saponification and to be susceptible of another explanation. As to the second argument, it may fairly be asked why the alcohol should be expected to dissolve the unchanged butter, when Mr. Wanklyn did not succeed in dissolving the far more soluble calcium butyrate by repeated treatments with water and alcohol? But is Mr. Wanklyn *quite sure* that no unchanged butter was dissolved out by the treatment with alcohol? He got a total alcoholic residue of 4·606 grms., or 9·212 per cent, and of this 3·201 grms., or 6·402 per cent, was insoluble in water. This portion presumably consisted of calcium salts of higher fatty acids; but how does Mr. Wanklyn know that it contained no admixture of un-changed butter? He does not say that he determined the lime in it or examined it in any other way.

The same doubt applies to the insoluble lime salts remaining after treatment of the product with water and alcohol, which Mr. Wanklyn appears to have left un-examined. It is to be regretted that he did not take the obvious precaution of decomposing these insoluble lime salts with acid, and seeing how far the fatty substance which separated consisted of free fatty acid, and how far of unchanged glyceride. But possibly Mr. Wanklyn's omission to do this was due to his peculiar and strictly personal difficulty in distinguishing a free fatty acid from a glyceride; for in the discussion on the very paper, " On the Constitution of Butter," in which Mr. Wanklyn described his lime experiment, he declined to pronounce an opinion as to whether or not butter-fat contained free fatty acids! (*Journ. Soc. Chem. Ind.*, x., 92). I trust Mr. Wanklyn will forgive the suggestion that the atten-tion he has given to other branches of chemistry has prevented him from keeping abreast with the improve-ments in the analytical methods of examining fats which have been so numerous during the last few years; one of which, in daily use in many laboratories, would have enabled him to detect and determine the proportion (in terms of any acid he might prefer) of free fatty acids in-side of twenty minutes.

So far I have purposely confined myself to a criticism of Mr. Wanklyn's one experiment: I next propose to describe my own experience in repeating it, and the other experiments which have suggested themselves in con-nection with it.

Sheffield, November 16, 1891.

DETERMINATION OF FATTY MATTER IN DAIRY PRODUCE.

By MM. LEZÉ and ALLARD.

IN the Session of March 24th, 1890, M. Lezê communi-cated to the Academy of Sciences a new process for determining the fatty acid of milk.

This process consists in heating in a flask a mixture of the milk to be analysed with 4 or 5 vols. of pure concen-trated hydrochloric acid; the caseine which is at first precipitated re-dissolves in the excess of acid, the fatty matter is isolated and collects in oily drops on the surface of the liquid. The acid is then neutralised with ammonia diluted with half its volume of water, and so much warm water is added that all the fatty matter appears in the neck of the flask.

This neck, which must be narrow and long, is divided into c.c.'s and tenths of a c.c.; the flask is kept for some time in a stove at 40°, and the volume of the fatty matter is read off, which, mutiplied by the specific gravity of this matter at +40°, gives the weight of butter for like of milk.

The temperature of +40° has been selected because at this heat the butter remains melted and homogeneous; its density is then =0·90.

The author's recent researches have been directed to the generalisation of this process for the determination of the fatty matter.

We have recognised at first that the separation of the fatty matter is always effected better if, in the treatment with hydrochloric acid, the acid is allowed to react upon the milk for several hours, preferably at a temperature of 25° to 30°. The reactions of caseine always take place slowly, and too hasty heating of the mixture of the two liquids when recently formed may cause an imperfect separation. The gentle heat merely collects the drops of the liquefied fatty matter.

The hydrochloric acid must be absolutely free from un-combined chlorine: if this condition is not observed there ensues a precipitation of flocculent matter and an escape of gas, which render it more difficult to read off the volume of the butter. The neutralisation with ammonia may be dispensed with, and smaller flasks may be employed.

We have examined if the fatty matter was really butter and had not undergone any chemical modification. In the stove it undergoes merely an insignificant loss; no trace of water is separated, and no residue is left on incineration.

We have found that by means of this reaction we may easily determine the fatty matter in creams, cheeses, and in margarines.—*Comptes Rendus* (vol. cxiii., p. 654).

ARSENICAL WINE.

IN a document handed in to a recent " Œcumenica Congress " the Editor of an influential London literary journal complained that " the modern mind had so steeped itself in Science that its faculties in other directions were blunted." But we may well question whether this steeping has led to saturation if we read the report of a late coroner's inquest in Sussex. A gamekeeper had obtained possession of an empty arsenic cask, and, as a medical contemporary informs us, utilised it for the storage of some home-made wine! The liquid took up, in consequence, nearly 6 grs. of arsenic per fluid ounce, and the first glass imbibed proved fatal.

On the inquest it appeared that the cask had contained a preparation known as " weed-killer." Large quantities of arsenic, it was stated, are used for this purpose by gardeners and farmers. Gamekeepers are not generally reputed as being the most enlightened part of Her Majesty's subjects—witness the sages who contended that the cuckoos all turned into hawks at the end of summer. But in ignorant recklessness the Sussex victim certainly deserves distinction.

But for such casks to be in the hands of an ignorant rural population is a great misfortune. Arsenic, no doubt, will kill weeds and the Colorado beetle as readily as it will gamekeepers. But there are other safer and equally convenient preparations which will rid garden-paths of weeds. As an instance we may mention the dregs from the preparation and storage of "nitrate of iron." This preparation, which is sometimes too abun-dant at chemical works, might safely be sold as a weed-killer. That it will destroy vegetation we know from observation, whilst if it should be accidentally scattered upon any esculent fruit or vegetable it can do little harm, especially as its abominably astringent taste would at once cause its rejection. But if the dust of an arsenical preparation is scattered over fruits and vegetables, neither the taste nor the colour will give any warning.

We quite agree with the suggestion of the Sussex jury that casks containing arsenic or arsenical preparations should be branded as a warning against their use after-wards. But the substitution of a less deadly preparation for horticultural and agricultural uses would certainly be a " more excellent way."

DETERMINATION OF SMALL QUANTITIES OF ALKALI AND RECOGNITION OF THE NEUTRALITY OF WATER.

By F. MYLIUS and F. FOERSTER.

(Continued from p. 255).

Preparation of the Solutions necessary for the Colorimetric Determination of Alkali.

THE first step is the preparation of pure ether. The ether of commerce is ordinarily acid. Its purification is generally effected by shaking with dilute soda-lye. Besides acids other impurities are thus removed. The ether thus treated is then once more shaken up with water and preserved over water, as it is used only in an aqueous state. It is then easily possible to remove by shaking any trace of acid which has been formed on long standing. The formation of acid takes place very slowly, so that it cannot occasion any error during the course of an operation. For preparing the ethereal solution of eosine 0·1 grm. of the pulverised colouring-matter, previously dried at 100°, is dissolved in 1 litre of aqueous ether. The solution requires several hours. If there are added to the solution a few c.c. of water they must assume on shaking a red tone in proof of the absence of acid. An alkaline solution of eosine is also necessary for effecting the colorimetric determination. It is obtained by dissolving 0·01 grm. iodeosine in a small excess of soda-lye (0·24 c.c., using 0·4 c.c. of 4-10ths soda-lye) and diluting the solution with water to 1 litre. If exposed to light it is decolourised in time, and must therefore be kept in brown bottles in a dark place.

For our experiments it was necessary to procure neutral water. For this purpose we used a distillatory apparatus of the following construction:—A round platinum flask containing 200 c.c. is connected at the top by means of a capital with a refrigerating worm. This consists also of platinum, so that the water during refrigeration comes in contact with no other material. The flask is heated by an annular burner. It terminates below in a platinum tube bent at right angles, connected at a convenient point with the efflux tube of a glass flask, which is also bent at right angles. Both vessels are at the same level, so that the height of the water in the glass vessel shows that in the platinum flask. A continual influx of water during the distillation is effected by a large Mariotte's vessel, the outflow tube of which is at the constant level.

If the apparatus is fed with distilled water, the distillate obtained, if collected in a platinum vessel, is free from solid impurities, but contains demonstrable traces of ammonia. To keep these back a small addition of sulphuric acid or of an acid sulphate is commonly employed. Phosphoric acid is unsuitable. If the water to be distilled was acidulated with a solution of vitreous phosphoric acid so as to redden litmus-paper distinctly, the first portions of the distillate were almost free from ammonia; but as the distillation continued, and the meta-phosphoric acid passed into ortho-phosphoric acid, the distillate became gradually richer in ammonia, so as to excite the suspicion that the vitreous phosphoric acid contained ammonia as an impurity. This was in fact the case, as Nessler's reagent gave the characteristic brown colour in the alkaline solution of the acid.

In our experiments 0·05 grm. pure sulphuric acid were quite sufficient to keep back the volatile bases in the platinum vessel even when the distillate amounted to several litres. Water thus obtained takes up, according to a number of experiments, for 100 c.c. as much eosine (0·054 m.grm.) as corresponds to 5·4 c.c. of the alkaline solution of eosine.

The objection might be raised that in our process a small portion of the sulphuric acid might have been carried over with the watery vapour. We sought to meet this objection by re-distilling the water in the same apparatus with pure soda. Repeated experiments showed

that the water thus re-distilled had the same eosine value as that distilled with sulphuric acid. The colour obtained in the eosine test corresponded on the average to 5·9 c.c. of the alkaline eosine solution. The difference of 0·5 c.c. which appeared on testing both kinds of distillates corresponds very closely to the mean experimental error, so it may be assumed that no appreciable transfer of sulphuric acid or of soda takes place during distillation. If a trace of sulphuric acid passes over it is certainly less than 100,000,000th part of the water.

We have hitherto not taken especial note of the impurities which the water takes up as it drops from the ambient air. We may call a water neutral which on the eosine test, according to our method, becomes coloured like a liquid which in 100 c.c. contains 5·65 of the alkaline solution of iodeosine.

In carrying out the more delicate alkalimetric investigations, it is often inconvenient first to procure pure water by distillation. It is generally sufficient to neutralise ordinary distilled water with sulphuric acid, so as to reach the "eosine value" of neutral water (5·6—5·7 c.c. of eosine solution in 100 c.c. of water).

The colorimetric determinations are best effected as follows:—Into a globular parting funnel holding about 150 c.c. there are introduced 100 c.c. of the water in question; 20 c.c. of the ethereal solution of eosine are added and well shaken. The aqueous reddened stratum is thus enlarged by taking up ether to 110 c.c.

(To be continued.)

ON THE ESTIMATION OF SULPHUR.

By GEORGE CRAIG.

EVOLUTION methods, whereby the substance to be determined is first of all eliminated as a gas from the material under examination, must always be more satisfactory than gravimetric methods, although no greater degree of accuracy is attained thereby. Such, for instance, is the estimation of NH_3 by liberation with alkali, with subsequent condensation and titration with standard acid,

Sulphur, when it exists as monosulphide, decomposable by HCl, is certainly best determined after expulsion as H_2S.

Pig-iron and steel, even when containing Cu, yield all their S as H_2S on treatment with HCl, which, as I proposed in 1881, may be completely oxidised to SO_3 by passing the gases through ammoniacal H_2O_2.

In blast-furnace slags the S exists wholly as CaS, which, it must be borne in mind, readily oxidises when the finely ground slag, especially from hematite iron, is kept for any time. The only correct method whereby it can be estimated, unless with the expenditure of much time and labour, is by decomposing the slag with HCl and estimating the S in the H_2S evolved. For this purpose I use the apparatus shown in Fig. 1, which scarcely needs explanation. 20 grs. of finely ground slag is heated with 1 oz. of boiled water, and the air expelled from the flask by a current of coal-gas which has been passed through a mixture of KHO and H_2O_2 in the Liebig's bulbs shown. When boiling agitate so that the slag is all in suspension, and add HCl by means of the 3-way stopcock, continuing the agitation until the slag is all decomposed, which takes place in a few seconds; boil, and pass a current of the purified coal-gas through the apparatus with the aid of the aspirator. The nitrogen bulb—containing 100 grs. H_2O_2, 200 grs. NH_4HO—is preferably made, as in figure, by cutting the escape-tube nearly at the bulb, widening the orifice, introducing some glass beads, and connecting with I.R. tubing as shown. The contents of the nitrogen bulb are washed into a small beaker, heated to boiling, acidified, and the SO_3 established as $BaSO_4$ as usual.

It is now more than a year since it occurred to me that

FIG. 1.
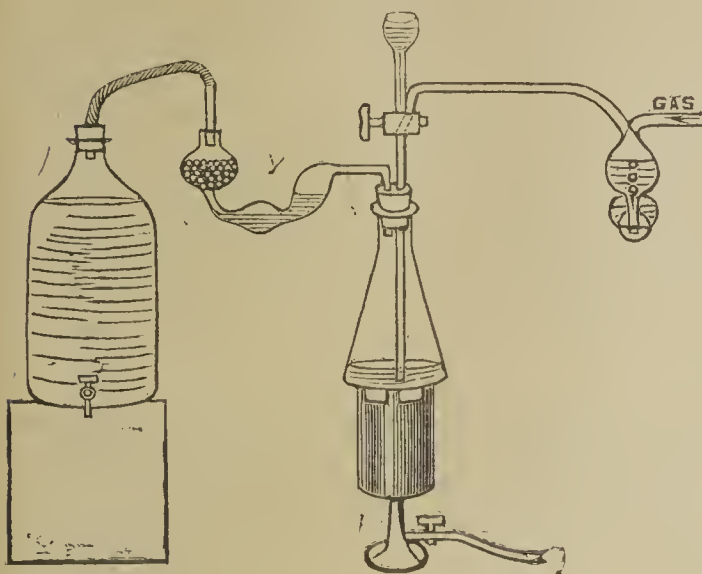
FIG. 2.
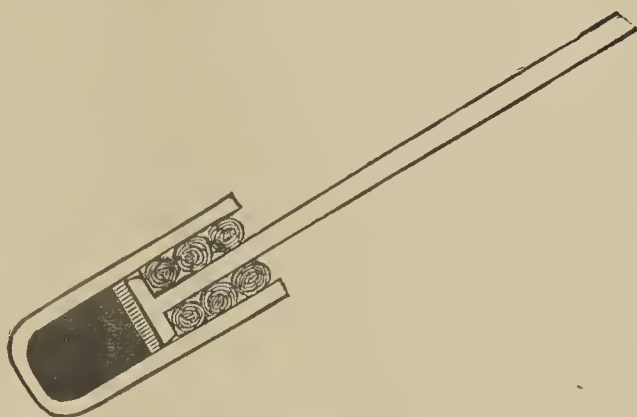
FIG. 3.
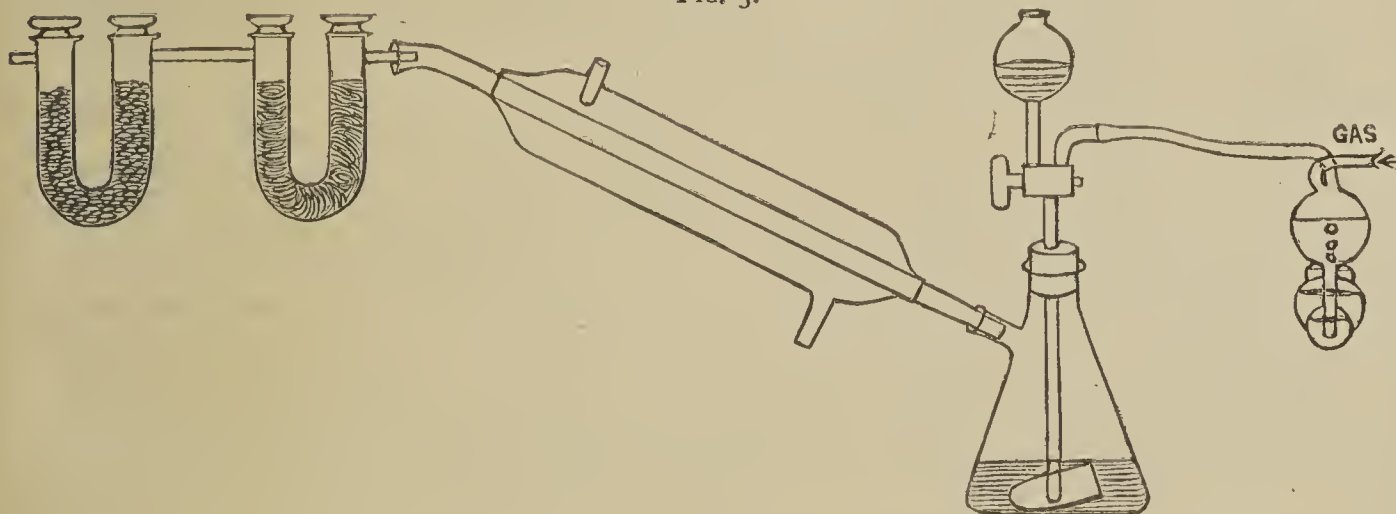
compound sulphides, such as pyrites, &c., might be made amenable to this evolution process also, by the simple preliminary operation of heating with zinc-dust, and so reducing to the state of monosulphides. In a recent number of the CHEMICAL NEWS there is a translation from the *Berichte* of an almost identical process; but as reduction with zinc is very much simpler, a description of the method I employed may be of interest.

Ordinary zinc-dust, after passing through a fine sieve, is heated to redness to expel moisture and occluded hydrogen, and allowed to cool out of contact with air; a tube of Bohemian glass closed at one end suits admirably for this purpose.

Ten or twenty grs. of the pyrites in fine powder are weighed into a small ignition tube of Bohemian glass (2″ long. × ½″ diam.), then five times its weight of zinc-dust added, intimately mixed with a platinum wire, the surface levelled by tapping gently, and covered with a layer of zinc-dust. A stout glass rod, about 8″ long, had one end flattened out into a disc that entered easily into the little decomposing tube. This was introduced until the disc rested lightly an the covering layer of zinc-dust, and the upper portion of the tube was packed with asbestos yarn firmly enough to enable the glass rod to serve as a support (Fig. 2). The tube and contents is then revolved over an argand flame until thoroughly heated, and then over a Bunsen flame. In a few seconds bright incandescence takes place, and after maintaining at a red-heat for thirty seconds longer it is withdrawn gradually, revolving all the while, and then allowed to cool.

When carried out in this manner practically no sulphate is reduced, but when maintained at a red-heat for five to ten minutes all sulphates are reduced. Apropos of sulphates in pyrites, I have not seen it recorded that a considerable amount of pyrites may be oxidised while grinding the sample in the agate mortar; in the dark a red glow follows the track of the pestle.

After withdrawing the support and asbestos packing the tube is dropped into a 4-oz. conical flask with side-tube, connected with condenser and U-tubes, as shown in Fig. 3. The first U-tube contains $CaCl_2$, and the second is filled with glass beads and contains 100 grs. of NaHO solution (1000 grs. and 1500 grs. water). 1 oz. boiled water is added, and a current of purified coal-gas passed through apparatus. Heat is applied and the HCl gradually run in until decomposed, contents boiled, and apparatus washed out with a current of gas. I preferred to estimate the H_2S by washing out the U-tube (without removing stoppers) into a beaker, adding excess of $FeCl_3$, agitating, acidifying with HCl delivered at bottom of liquid by means of a pipette, heating until all FeS decomposed, and titrating with bichrome. The ideal process would be to accurately weigh the NaHO solution and titrate after absorption with acid, using an indicator neutral to NaHS or Na_2S. The arsenic I found was completely expelled, so that not a trace could be detected in the combined residues from a number of experiments.

Lugar Iron Works, Cumnock N.B.,
    November 19, 1891.

PROPERTIES OF PRECIPITATES, &c.*

By E. WALLER, Ph.D.

(Continued from p. 259).

$PbCrO_4$.

Rem.—Usual precipitant, $K_2Cr_2O_7$ in solution acid with acetic.

Cond. — Bi, Ba, Ag, and Fe should not be present. Solution should not contain chlorides or large amounts of alkaline salts, and should be acid with no stronger acid than acetic. Alkaline citrates, tartrates, &c., should be absent.

Sol.—Dissolved by moderately strong mineral acids and by caustic alkalies. HCl reduces the chromium partially or entirely to Cr_2Cl_6, more readily in the presence of acetic acid, alcohol, or other carbon compounds. Soluble in hot moderately concentrated solutions of $(NH_4)C_2H_3O_2$. Insoluble in very dilute HNO_3.

Contam.—Possibly Ba, Bi, or Hg, chromates, &c. If much Fe is present, the precipitate is likely to contain that element, probably as $Fe_2(CrO_4)_3$.

Ign.—Alone fuses and parts with some oxygen. With C it is more easily decomposed, some metal being reduced. On account of these properties the precipitate is usually dried on a weighed filter for estimation. The Gooch filter, in which, if paper is used, it need be only about the size of a five cent piece, is especially advantageous for this purpose.

PbS.

Rem.—Usual precipitant, H_2S. Partially decomposed by drying at 100° C. Used for separation.

Cond.—Solution may be slightly acid, neutral, or alkaline. HCl interferes most with complete separation, HNO_3 less, and H_2SO_4 least. If the solution is acid with any large proportion of these, the precipitation is best effected in the cold.

Sol.—Dissolved by dilute boiling HNO_3, though that solvent almost invariably affords some $PbSO_4$. Of concentrated acids hot HCl is the best solvent, since with either HNO_3 or H_2SO_4 some $PbSO_4$ will form in such a way as to protect a portion of the sulphide. Soluble in $Na_2S_2O_3$.

Ign.—Volatilised. Easily reduced to metal by ignition with C.

$AgCl$.

Rem. — For determination of Ag, usual precipitant HCl. For determination of Cl, usual precipitant $AgNO_3$. Separates most readily in presence of an excess of silver salts. Partially decomposed by heating with strong HNO_3 or H_2SO_4. Darkens in strong daylight, more quickly in sunlight, but may become very dark without material loss of weight.

Cond.—Acid solution, absence of any notable quantities of alkaline chlorides or other alkaline salts.

Sol.—Partially dissolved by moderately strong and hot HCl or HNO_3. Somewhat soluble in alkaline and alkaline earth chlorides and nitrates. Readily soluble in NH_4OH, in KCy, and in $Na_2S_2O_3$. In the latter, less readily if the substance has been changed by light.

Ign. — Fuses at a low temperature (dull red) and volatilises at a little higher temperature. Easily reduced to metal by strong heat, especially when mixed with Na_2CO_3 or C. On burning the filter-paper (which should be separated from the precipitate) the ash should be treated with HNO_3 to obtain $AgNO_3$, then a drop or two of HCl is added to restore AgCl, and the whole after drying cautiously heated to incipient fusion.

As_2S_3.

Rem.—Usually precipitated by H_2S in HCl acid solution. From the solution of arsenic sulphides in alkaline polysulphide, the addition of acid separates As_2S_5.

As_2S_3 requires very thorough drying before weighing, the last portions of water being driven out with difficulty.

Cond. — Solution acid, with some mineral acid (HCl preferable). As should be in triad form. If in pentad form it is slow to reduce and precipitate ($As_2S_3 + S_2$) by prolonged action of H_2S and warming.

Sol.—Dissolved by alkaline solutions (hydrates, carbonates, or sulphides), also by aqua regia, fuming nitric acid, water solutions of chlorine, bromine, &c. In a neutral solution scarcely any precipitation occurs. Insoluble in strong HCl, even on boiling. Practically insoluble in H_2SO_4. Dissolved by $KHSO_3$.

Ign.—Readily volatilised without change of composition.

$MgNH_4AsO_4$.

Rem.—Usual precipitant, $MgCl_2$ in ammonia solution containing alcohol. Precipitate white, crystalline closely resembling $MgNH_4PO_4$.

Cond.—Solution alkaline with ammonia, containing a minimum amount of NH_4Cl and 25 to 30 per cent of alcohol. No sulphates or other compounds, partially or entirely insoluble in alcohol of this strength, should be present. The As must be in pentad form (a condition realised in solutions containing alkaline polysulphides).

Sol.—Dissolved by acids or on application of heat. Somewhat soluble in water and in NH_4Cl, an effect partly neutralised by presence of ammonia and alcohol, in which it is insoluble.

Contam.—Basic Mg salts, sulphates, and other salts partially or entirely insoluble in diluted alcohol.

Ign.—Partially volatilised if heated up quickly. By slow heating it is dried and finally altered to $Mg_2As_2O_7$, which is non-volatile. With C partly volatile. A convenient method of management consists in dissolving the washed precipitate through the filter by dilute HNO_3 into a weighed capsule, evaporating, igniting slowly and finally intensely.

Sb_2S_3.

Rem.—Usually precipitated by H_2S in acid solution, or by acidifying solutions of sulphantimonite.

On drying, the precipitate does not surrender all H_2O until the temperature is raised to 200° C., when it becomes black. This degree of heat is liable to char the paper when dried on a weighed filter.

By the action of oxidising agents (Br, HNO_3, HgO, &c.) it is converted to Sb_2O_4.

Cond.—Solution slightly acid and moderately dilute. An excess of H_2S causes a more rapid separation of the precipitate. If too acid or too concentrated the precipitation may be imperfect.

Sol.—Precipitate dissolved or prevented from forming by moderately concentrated acids, especially HCl. H_2SO_4 has much less effect. The preventive effect is increased with the temperature. Tartaric acid in the solution assists precipitation.

Dissolved by fixed alkalies or alkaline sulphides.

Scarcely soluble in ammonium carbonate or $KHSO_3$.

Somewhat soluble in $H_2C_2O_4$, but insoluble in it if boiled in presence of an excess of H_2S. (Separation from tin.)

Contam.—S usually accompanies the precipitate. To remove this the water is first displaced by alcohol, and the S dissolved out by CS_2.

Ign.—Partially or entirely volatilised by ignition alone or by reducing agents. Mixed with 30 to 50 times its weight of HgO and ignited, it is converted to Sb_2O_4, which is stable at the ordinary temperature of ignition. Frequently, however, it is converted to Sb_2O_4 by Br or HNO_3 before ignition.

$H_{10}Sn_5O_{15}$ or $5(H_2SnO_3)$.

Rem.—The above is called the "insoluble" form of hydrated stannic oxide, because not readily soluble. It is usually obtained by boiling slightly acid (HNO_3 or H_2SO_4) solutions containing the soluble form in partial

suspension, or by boiling weakly acid solutions (of stannic compounds) containing neutral alkaline salts (NH_4NO_3, $NaNO_3$, Na_2SO_4, &c.). The presence of acetates assists the separation.

Cond.—HCl or chlorides should be small in amount, preferably entirely absent. Solution should be acid, tolerably dilute, and boiled for some time.

Sol.—The "soluble" form (obtained by neutralising stannic solutions with caustic or carbonated fixed alkalies) is readily soluble in excess of the alkali or in acids. The "insoluble" form is only soluble with difficulty in HCl or in caustic alkali, and practically insoluble in dilute HNO_3 or H_2SO_4.

Contam.—As and Sb oxides, which should have been removed previously. In analyses of bronzes, &c., CuO removed by long digestion with dilute HNO_3. SiO_2, removable by treatment with HFl and H_2SO_4. Fe_2O_3, removed by fusion with NaOH or Na_2CO_3, and, after further treatment by well-known methods, separating the Fe_2O_3, which is weighed and deducted. This operation is usually performed upon a *weighed portion* of the precipitate.

Ign.—Requires intense heating to remove all H_2O. Not easily reduced to (volatile) Sn by C, though such reduction is possible on igniting the precipitate. Volatilised as chloride by ignition with NH_4Cl. Otherwise not volatile at high temperatures.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.
November 5th, 1891.

Mr. W. CROOKES, F.R.S., Vice-President, in the Chair.

Mr. J. Tudor Cundall was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. George James Allen, Ivy House, Bolton Road, Pendleton; George Alfred Ashcroft, 88, Alexandra Road, Manchester; Harold Alger, The Manor House, Stoke, Devonport; Edward Charles C. Baly, Bank of England; Thomas William Berry, Shireoaks, Worksop, Notts; Samuel Francis Burford, Eastleigh, Queen's Road, Leicester; John Bairstow, 32, Sealand Road, Chester; J. Treeby Barratt, Mostyn, North Wales; John Redman Bovell, Dodds, Barbados; John C. Chorley, Lodge Lane, Bewsey, Warrington; George Edward Cory, The Public School, Grahamstown, South Africa; Thomas Darling, 1, Palace Street E., Berwick-on-Tweed; Charles E. Eastick, Myrtle Bank, Leyton; Percy Elford, Christ Church, Oxford; Lionel William Fulcher, 37, Melford Road, Lordship Lane, S.E.; George German, Jun., Aseby-de-la-Zouch; Alfred Daniel Hall, Martyn Road, Guildford; Archibald Hall, 34, Bishopsgate Street; John Holliday, 7, Aglionby Street, Carlisle; John Walter Leather, 15, Bradgate Road, Catford, S.E.; Lionel Ludlow, 90, Walter Road, Swansea; John Willis Marshall, 10, Palatine Square, Burnley; Daniel McLaren, B.Sc., 30, Raleigh Street, Nottingham; Joseph Morris, Stamford Street, Mossley, near Manchester; William Naylor, 182, Newhampton Road, Wolverhampton; Thos. Neilson, 26, Harrington Road, Workington, Cumberland; Abhayacharan Sauyal, M.A., Muir Central College, Allahabad; Walter Thorp, 3, Melbourne Villas, Headingley, Leeds; A. W. Winterton, 6, Lindum Terrace, Rotherham; John Henry Wilson, 29, Radford Street, Coventry.

The following papers were read:—

59. "*The Magnetic Rotatory Power of Solutions of Ammonium and Sodium Salts of some of the Fatty Acids.*" By W. H. PERKIN, Ph.D., F.R.S.

Ostwald, in his paper on magnetic rotation (*C. S. Trans.*, 1891, 198) has argued that the peculiar results obtained by the author in the case of solutions of acids and of ammonium salts, &c., are in accordance with the electrolytic dissociation hypothesis; and has suggested that, since salts formed from weak acids are as good conductors as those formed from strong ones, we may expect in this case, also, marked deviations from the calculated values. The same chemist, in his work on Solutions, considers that there can be no doubt that such salts as ammonium formate, &c., when in aqueous solution, would show molecular rotations which would not be the sums of the rotations of the components of the salts, as must (nearly) be the case if the view put forward by the author be correct, that such salts are almost entirely dissociated into acid and base. Experiments made with the object of throwing further light on the subject have afforded the following results:—

		Mols. Water to 1 mol. Salt.	Mol. Rot.	Average Mol. Rot.
Ammonium formate	..	3·00	3·363	
,,	,, ..	8·78	3·394	
,,	,, ..	10·00	3·333	3·363
,,	acetate ..	4·75	4·246	
,,	,, ..	13·13	4·247	4·246
,,	propionate	2·86	5·255	
,,	,, ..	10·26	5·263	5·259
Sodium formate	.. ..	5·40	2·364	
,,	,, ..	12·54	2·331	2·347
,,	acetate ..	11·23	3·281	3·281
,,	propionate ..	7·00	4·308	4·308
,,	butyrate.. ..	6·81	5·332	5·332

It will be seen that the rotatory powers of the ammonium salts do not vary with dilution; there can be little doubt that this is true also of the sodium salts, as sodium formate shows no difference on dilution. Comparing the experimental values obtained in the case of the ammonium salts with those afforded by the constituent acid and ammonia, the following results are obtained:—

CH_2O_2 ..	1·671	$C_2H_4O_2$ ..	2·525	$C_3H_6O_2$	3·462
NH_3 ..	1·818		1·818		1·818
	———		———		———
	3·489		4·343		5·280
Am. salt..	3·363		4·246		5·259
	———		———		———
Diff. ...	0·126		0·095		0·021

As might be expected, as reduction of rotatory power always attends combination, the values are slightly less in the case of the salts. The author points out that the reduction is very nearly the same as that which takes place in the formation of the corresponding ethereal salts, and as these salts are anhydrous the results may be held to justify the conclusion that the values obtained for ammonium salts in solution are practically those of the dry salts, and therefore that Ostwald's views are inapplicable. In the case of sodium salts it is more difficult to arrive at a conclusion, as the value of sodium is unknown, but it is shown that whatever influence water has on them it is to be supposed that it acts to the same extent on all the four salts examined.

60. "*Note on the Action of Water Gas on Iron.*" By Sir H. E. ROSCOE and FRANK SCUDDER.

During some experiments which the authors have recently been making on the application of water gas for illuminating purposes by means of the well-known Fahnehjelm system, it was occasionally observed that after the water gas had impinged on the comb for some hours a deposition of ferric oxide was formed on the magnesia rods, the result being that the illuminating power was considerably lowered.

It was at first suggested that the iron came from the particles of dust which were present in the atmosphere of the steel works where these experiments were being conducted. Further examination of the tips of the steatite

burners showed, however, that the deposit of ferric oxide was " coralloid," and that, therefore, it could not be produced from dust in the atmosphere, but was contained in the gas itself. In order to ascertain whether the iron was in a gaseous state or in the form of finely divided particles, the gas was filtered through several tight plugs of cotton wool; but as a similar deposit was observed after four or five hours, it was concluded that the water gas contained a volatile iron compound.

These facts, although interesting, only showed that the quantity of the volatile iron compound was extremely small, apparently precluding all hope of extracting sufficient of the material for analysis. Nevertheless the occurrence of iron, even in these minute quantities, was a most serious bar to the technical application of water gas as an illuminant, and the question of its origin as well as its removal became of practical interest.

In the course of experiments made for another purpose, water gas was compressed in steel cylinders to a pressure of 8 atmospheres, and on burning the gas immediately after compression no visible alteration in the colour of the flame or in the amount of iron contained in the gas was observable; but after the compressed gas had remained in the cylinders for about a month, it was found that when it was burned from a steatite burner the flame was highly luminous, and instantly deposited on the Fahnehjelm comb a yellowish red coating of ferric oxide: proving that a much larger quantity of iron was contained in the gas which had been kept than in the original compressed gas.

On passing a small quantity of the gas through a piece of combustion tubing heated externally by a Bunsen burner, a large deep black mirror was rapidly formed, which proved on analysis to be metallic iron, free from carbon, arsenic, and antimony.

The flame, however, still remained strongly luminous, particles of metallic iron burning brightly in it, whilst either a black mirror of metal or one of ferric oxide was deposited on a porcelain plate held above it according to the position in which the plate was held. On inserting a plug of cotton wool between the heated portion of the tube and the burner, the flame instantly became non-luminous, and in a few seconds the cotton wool nearest to the heated part of the tube became black; in a short time the whole plug was deeply stained with finely divided metal. Hence it was evident that under a pressure of 8 atmospheres the carbonic oxide contained in water gas (about 39 per cent of its bulk) slowly attacked metallic iron at the ordinary atmospheric temperature.

In a preliminary determination in which about 30 litres of gas was burned in half an hour, the weight of the metallic iron deposited as a mirror amounted to 0·0322 grm., whilst that found on the plug of cotton wool was 0·0406 grm., a total of 0·0728 grm. of iron, equal to 2·4 m.grms. per litre.

Although the compound, which is, doubtless, the iron carbonyl of Mond and Quincke, is only present in this small quantity, the authors have found that it can readily be liquefied if the gas be passed through a cotton-plugged tube and then led into a U-tube surrounded by a mixture of salt and ice: a few drops of turbid liquid thus deposited became clear on treatment with a little hydrochloric acid, and on adding potassium ferrocyanide a deep blue colour was obtained.

The authors hope, before long, to communicate more detailed information as to the causes of the occasional occurrence of the volatile iron compound in water gas, and as to its nature. The action of water gas on other metals will also receive their attention.

DISCUSSION.

The CHAIRMAN referred to the fact that at the recent British Association Meeting at Cardiff Mr. Mond had exhibited specimens not only of liquid iron carbonyl, but also of a solid compound of iron with carbonic oxide.

Prof. RAMSAY stated that he had found that the com-

pound of nickel with carbonic oxide was formed in the cold, the action frequently going on for days. He subsequently added, in reply to a question by Mr. Groves whether dry pure carbonic oxide acted on iron, that in the case of nickel, the gas acted equally well when dried by phosphoric anhydride.

Sir Henry Roscoe, in the course of his account, had mentioned that ordinary coal gas contained traces of iron, pointing out that this was the cause of the stain observed on steatite burners. Referring to this point, Dr. THORNE mentioned that he had recently had occasion to detect iron in compressed coal gas, which was now frequently used for the production of the limelight. In using such gas it was sometimes noticed that the lime cylinder acquired a brown deposit, and it was owing to this circumstance that he was led to examine the gas.

61. " *The Dissociation of Liquid Nitrogen Peroxide.*" By J. TUDOR CUNDALL, B.Sc., Lecturer on Chemistry in the Edinburgh Academy.

The author has determined, by colorimetric methods, the relative amount of NO_2 formed in liquid nitrogen peroxide (i.) by dilution with chloroform, (ii.) by rise of temperature. He has also ascertained the absolute amount of dioxide by comparing the colour of the liquid solution with that of the gas containing a known amount of nitrogen dioxide. The results go to show that, on dilution, (i.) dissociation takes place very slowly at first, but more rapidly when less than 5 per cent of the peroxide is taken; (ii.) that solutions of the peroxide dissociate more rapidly than the pure liquid on rise of temperature. In the most dissociated solution yet examined, viz., one to which had been added 1·44 per cent of peroxide by vol. at 25° C., not more than 1·22 per cent of NO_2 was present.

DISCUSSION.

Prof. RAMSAY pointed out that the fact established by Mr. Cundall, that nitrogen peroxide was dissociated to but a slight extent on dilution unless the solution were very dilute, was a confirmation of the result which he had obtained on determining the molecular weight of the peroxide by Raoult's method.

Prof. THORPE suggested that the rate of dissociation might possibly be ascertained by determining the relative densities of solutions of nitrogen peroxide at different temperatures.

Mr. CUNDALL thought that the variation was too slight to permit of the application of such a method.

62. " *Ortho- and Para-nitro-orthotoluidine.*" By ARTHUR G. GREEN and THOS. A. LAWSON, Ph.D.

It has been shown by Nölting and Collin (*Ber.*, 1884, 265) that when orthotoluidine sulphate is nitrated at a low temperature in presence of a large excess of sulphuric acid, *para*-nitro-orthotoluidine,—

$$C_6H_3Me(NH_2)(NO_2) \ [1:2:4],$$
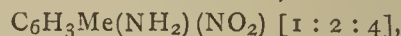
results. This isomer appears to have been considered to be the only product of the interaction under these conditions, but the authors have found that this is by no means the case, for besides the para-nitro-orthotoluidine (about 75 per cent) there is formed about 3 or 4 per cent of *meta*-nitro orthotoluidine,—

$$C_6H_3Me(NH_2)(NO_2) \ [1:2:5],$$
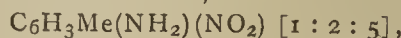
and about 20 per cent of *ortho*-nitro-orthotoluidine,—

$$C_6H_3Me(NH_2)(NO_2) \ [1:2:6].$$
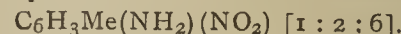
The latter, which up to the present has only been obtained by reduction of the consecutive dinitrotoluene, like para-nitro-orthotoluidine, has the NH_2 and NO_2 groups relatively in the meta-position, and hence the simultaneous formation of these two isomers (the 1 : 2 : 6 and the 1 : 2 : 4) by nitration of orthotoluidine in presence of sulphuric acid might have been theoretically expected.

The separation of the orthonitro-orthotoluidine from the mixture is effected by taking advantage of the greater solubility of this isomer in slightly warm water.

	1:2:4	1:2:6
CH_3 NH_2 NO_2	M.p. 107° (Nölting and Collin), 107·5°, very sharp, yellowish needles; very sweet taste.	M. p. 91·5° (Bernthsen) (G. and L.). Fine, light-yellow needles; not sweet.
CH_3 OH NO_2	M. p. 107 to 108° (Nölting and Collin). Fine, yellowish needles; very sweet taste.	M. p. 142 to 143° (Uhlmann), 105° (G. and L.). Prisms.
CH_3 NH_2 NH_2	M.p. 99°. Prismatic crystals.	M. p. 103·5° (Uhlmann), 105° (G. and L.). Prisms.
CH_3 $NHAc$ $NHAc$	M. p. 221°, (Tiemann), 224° (Ladenburg). Does not sublime in flocks. Orange prisms; very sweet taste.	M. p. 202 to 203° (G. and L.). Pale-yellow plates. Sublimes in very light flocks.
CH_3 NH_2 N_2O	M. p. 168° (Limpricht), (G. and L.). Small, white needles.	M. p. 149° (G. and L.). Yellow needles or orange prisms.
CH_3 $NHAc$ N_2O	M. p. 290° (G. and L.). Small, white prismatic needles.	M. p. 197° (Limpricht), 203° (G. and L.). Orange, prismatic needles.
CH_3 NH_2 N_2	M. p. 307° (G. and L.). Small, white, flat needles.	M. p. 175° (G. and L.). Orange plates.
CH_3 $NHAc$ N_2	M. p. 300° (G. and L.). Long, white needles.	M. p. above 340° (G. and L.). Small, yellow needles.
CH_3 Cl NO_2	M. p. 65·5° (Wachendorff), 137° (Wachendorff). Long, white needles.	M. p. 136 to 137° (Wachendorff).
CO_2H Cl NO_2	M. p. 37° (G. and L.). White, prismatic needles.	M. p. 161° (G. and L.). Compact, yellow needles; slightly sweet.

Having at their disposal considerable quantities of the ortho- and para-nitro-orthotoluidine, the authors have made a comparison of these two isomers and of their products of reduction and other derivatives, which is summarised in the foregoing table.

63. "*Researches on the Gums of the Arabin Group. Part II. Geddic Acids. Gedda Gums; the Dextrorotatory Varieties.*" By C. O'Sullivan.

The Gedda gums described consist of the calcium, magnesium, and potassium salts of gum acids, the calcium salt predominating, together with more or less nitrogenous matter, which is probably in some way combined with a true gum acid.

They dissolve easily in water, forming a yellow or reddish syrup, neutral to test-paper, which is dextrorotatory.

If the solution be acidified and dialysed for some time, the whole of the ash may be separated, and if alcohol be added carefully to the dialysed liquid, a powdery precipitate first separates which contains the whole of the nitrogenous bodies and some gum acid; on allowing the precipitate to deposit, and then decanting the clear supernatant liquid, and adding alcohol, a syrupy precipitate is obtained, consisting of a mixture of the gum acids present in the natural gum. By repeatedly fractionating the aqueous solution of these gum acids by alcohol, they were separated from one another and obtained in a pure state.

The gum acids contained in any one sample of gum bear a very simple relation to one another, and they are also intimately related to the gum acids contained in other samples. These relationships are indicated in Table I.

Of these gum acids, those having the highest molecular weight are most soluble in dilute alcohol.

The gum acid of gum arabic is similarly constituted, being, in fact, diarabinantetragalactanarabic acid,—

$$2C_{10}H_{16}O_8 \cdot 4C_{12}H_{20}O_{10} \cdot C_{23}H_{30}O_{18};$$
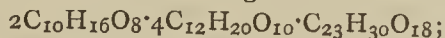
and the acids present in the third sample of Gedda gum described are similarly constituted, geddic and arabic acids being isomeric.

The composition and partial constitution of any one of the gum acids which have been as yet examined may be expressed by the general formula—

$$C_{23}H_{38-2n}O_{22-n} \cdot nC_{12}H_{20}O_{10} \cdot pC_{10}H_{16}O_8.$$
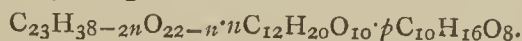
When a solution containing 2 per cent H_2SO_4 of any one of these gum acids is heated at 80—100° C. for ten to thirty minutes, the gum acid is hydrolysed, yielding arabinon and a gum acid of lower molecular weight, the whole of the arabinon residue indicated in the general formula being liberated. The change may be expressed as follows:—

$$C_{23}H_{38-2n}O_{22-n} \cdot nC_{12}H_{20}O_{10} \cdot pC_{10}H_{16}O_8 + pH_2O =$$
$$= C_{23}H_{38-2n}O_{22-n} \cdot nC_{12}H_{20}O_{10} + pC_{10}H_{18}O_9.$$
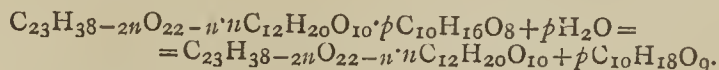
The greater portion of the arabinon thus produced is hydrolysed to arabinose, $C_{10}H_{18}O_9 + H_2O = 2C_5H_{10}O_5.$

It is possible by carefully restraining the hydrolytic action to obtain gum acids which still contain the arabinon residue, but, under the conditions given, practically the whole of the arabinose obtainable is produced.

The gum acids thus produced are separated from the sugars by treatment with alcohol; they very closely resemble the gum acids existing in the natural gums, but are less optically active and less soluble in weak alcohol.

As is evident from the formulæ given above, any one of the gum acids contained in a given sample of gum, when thus hydrolysed, yields the same gum acid; and the acids obtained from the natural acids of different samples are closely related together. This is indicated in Table II.

It is noteworthy that these acids bear a relation to one another similar to that of the different acids contained in any one sample of the natural gums. The most marked point of difference between these gum acids and those

TABLE I.

Name.	Formula.	[α]D.	P.c. BaO in Ba salt.
Gedda gum I.			
Tetrarabinantrigalactangeddic acid	$4C_{10}H_{16}O_8 \cdot 3C_{12}H_{20}O_{10} \cdot C_{23}H_{32}O_{19}$	+ 59°	5·59
Triarabinantrigalactangeddic acid	$3C_{10}H_{16}O_8 \cdot 3C_{12}H_{20}O_{10} \cdot C_{23}H_{32}O_{19}$	+ 49°	6·05
Diarabinantrigalactangeddic acid	$2C_{10}H_{16}O_8 \cdot 3C_{12}H_{20}O_{10} \cdot C_{23}H_{32}O_{19}$	+ 43°	6·75
Monarabinantrigalactangeddic acid	$C_{10}H_{16}O_8 \cdot 3C_{12}H_{20}O_{10} \cdot C_{23}H_{32}O_{19}$	+ 37°	7·65
Gedda gum II.			
Nonarabinantetragalactangeddic acid	$9C_{10}H_{16}O_8 \cdot 4C_{12}H_{20}O_{10} \cdot C_{23}H_{30}O_{18}$	+110°	3·46
Heptarabinantetragalactangeddic acid	$7C_{10}H_{16}O_8 \cdot 4C_{12}H_{20}O_{10} \cdot C_{23}H_{30}O_{18}$	+100°	3·93
Pentarabinantetragalactangeddic acid	$5C_{10}H_{16}O_8 \cdot 4C_{12}H_{20}O_{10} \cdot C_{23}H_{30}O_{18}$	+ 90°	4·55
Triarabinantetragalactangeddic acid	$3C_{10}H_{16}O_8 \cdot 4C_{12}H_{20}O_{10} \cdot C_{23}H_{30}O_{18}$	+ 80°	5·40

TABLE II.

Obtained by the action of sulphuric acid on the gum acids contained in—	Name.	Formula.	[α]D	P.c. BaO in Ba salt.
Gedda gum III.	Pentagalactangeddic acid.	$C_{23}H_{28}O_{17} \cdot 5C_{12}H_{20}O_{10}$	+30°	6·51
Gedda gum II.	Tetragalactangeddic acid.	$C_{23}H_{30}O_{18} \cdot 4C_{12}H_{20}O_{10}$	+22°	7·49
Gum arabic.				
Gedda gum I.	Trigalactangeddic acid.	$C_{23}H_{32}O_{19} \cdot 3C_{12}H_{20}O_{10}$	+20°	8·81

present in the natural gum is their behaviour when heated with a 2 per cent solution of sulphuric acid; they offer great resistance to the hydrolytic action of this acid, but are slowly broken down by several hours' digestion, the galactan residue being removed, and acids of successively lower weight being formed; the lowest stage is represented by the general equation—

$$C_{23}H_{38-2n}O_{22-n} \cdot nC_{12}H_{20}O_{10} + 3nH_2O =$$
$$= C_{23}H_{38}O_{22} + 2nC_6H_{12}O_6.$$
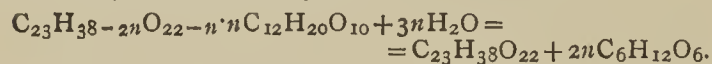
The properties of the compound $C_{23}H_{38}O_{22}$ have not yet been very accurately determined, the difficulty being to obtain a sufficient quantity.

This gum acid and the others obtained after the partial hydrolysis of the galactan residue can only be precipitated from their concentrated aqueous solutions by very strong alcohol; they are dialysable, and strongly acid.

Those obtained from Gedda gum are highly dextrorotatory, whilst those from gum arabic, although otherwise identical, are inactive.

64. "*Some Compounds of the Oxides of Silver and Lead.*" By EMILY ASTON, B.Sc.

The author finds that on following the directions given by Wöhler (*Pogg. Ann.*, 1837, xli., 344) for the preparation of the compound $Ag_2O,2PbO$, the product varies in composition, the highest percentage of silver obtainable being 49·01, whereas the amount required for Wöhler's compound is 34·23.

When a mixture of lead and silver hydroxides is allowed to stand in presence of caustic soda, a change of colour occurs, and after repeated extraction with caustic soda, a substance is left having a composition nearly that required by the formula $2Ag_2O,PbO$. A product of similar composition is obtained by precipitating the mixed nitrates of lead and silver, and exhaustively extracting with caustic soda.

Attempts to prepare compounds of lead oxide with the oxides of barium, strontium, sodium, and potassium were unsuccessful.

65. "*The Electrolysis of Potassium Acetate Solutions.*" By T. S. MURRAY, D.Sc.

On electrolysing a very dilute aqueous solution of potassium acetate, only hydrogen and oxygen are evolved; if the solution be a concentrated one, the gaseous product is a mixture of ethane, hydrogen, oxygen, methyl acetate (trace), and carbon dioxide: a portion of the carbon dioxide arises from oxidation of some part of the electrolyte, or product of the electrolysis.

The author has investigated the influence of concentration of solution, strength of current, size of electrodes, temperature, &c., on the course of the electrolysis. He

proves the absence from the gas of acetone, methyl oxide, ethylene, or any unsaturated hydrocarbon.

On diluting the solution of acetate, the amount of ethane produced decreases, at first very slowly, but finally with great rapidity. For instance:—

Per Cent.
A 60 solution gave ethane = 80·0 (hydrogen = 100).
  ,, 11·77   ,,   ,,   ,, = 73·5
  ,, 1·84   ,,   ,,   ,, = 50·8
  ,, 0·50   ,,   ,,   ,, = 0·003

Reducing the current has a similar influence. With rise of temperature, the ethane diminishes in quantity more rapidly the higher the temperature, and ceases to be formed at about 100° C.

In contradiction to Jahn, he finds that the employment of a large anode reduces the yield of ethane, the largest yield being obtained by the use of a very small anode; variations in the cathode do not influence the electrolysis. The presence of acetic acid, or of alkali, even in small quantity, reduces the yield of ethane.

The oxidation of the electrolyte to carbon dioxide, which proceeds simultaneously with the formation of ethane, is affected very differently by changes in the several conditions. Thus for a given yield of ethane = 25 say (hydrogen = 100), the corresponding oxidations produced are by change of current, 96; by varying size of anode, 68; by varying concentration, 60; by varying the temperature, 50; possible oxidation being taken as 100. With a yield of ethane about 75, no matter how it is obtained, the oxidation is always about the same, namely, 94.

The results of the investigation are illustrated by a series of curves. The author believes that he has demonstrated that the ethane is formed, not by a partial oxidation of acetic acid, as Bourgoin, Jahn, and Bunge believe, but that it results from a simple interaction of the acetions ($CH_3 \cdot COO$). He finds that the yields of ethane obtained from equivalent solutions of potassium, sodium, and calcium acetates are equal.

66. "*A New Method of Preparing β-Dinaphthylene Oxide and the Constitution of its Tetrasulphonic Acid.*" By W. R. HODGKINSON and L. LIMPACH.

The method in question is to heat the sodium salt of 2 : 3′-β-naphtholsulphonic acid (Schaefer's acid) to low redness; the distillate also contains β-naphthol and β-dinaphthyl ether: the former having been extracted by alkali, the residue is dissolved in acetic acid; as the solution cools the oxide separates as a yellow, fluorescent substance, and when recrystallised forms rhombic plates melting at 153°. Its picrate crystallises from alcohol in

dark red needles melting at 134. It is easily converted into a tetrasulphonic acid.

The same tetrasulphonic acid is formed by the continued action of sulphuric acid on β-naphthol.

CORRESPONDENCE.

BEEF FAT.

To the Editor of the Chemical News.

SIR,—In his letter (CHEMICAL NEWS, vol. lxiv., p. 224) Mr. A. H. Allen writes " For tallow read beef fat, which is practically synonymous, and my statement is absolutely correct." From that statement I totally dissent, and now deny ever having even mentioned caustic potash (KHO); for caustic potash read caustic soda (which, according to Mr. Allen, is practically synonymous), and my results are absolutely correct,—results which I am perfectly satisfied with, the accuracy of which no unprejudiced person would gainsay. I have, however, re-determined the fatty acids in the exact sample with the following results—94·42 and 94·48 per cent, results which agree remarkably well with the original estimations, which were as follows :— Fatty acids, 94·24 and 94·52 per cent; and the normal soda consumed by 2·5 grms. 10·54 and 10·57 c.c.

If one calculates the glyceryl (C_3H_2) from the amount of KHO consumed, we obtain—

$$C_3H_2 \quad .. \quad .. \quad .. \quad 5\cdot40$$
$$\text{Fatty acids} \quad .. \quad — \quad 94\cdot38$$
$$\overline{99\cdot78}$$

Results which were actually obtained from pure beef fat, even though ridiculed by your correspondent. Since the publication of the original results I have continued my investigation of the constitution of butter-fat, and am now in a position to announce that I have been enabled to separate butter-fat into two distinct glycerides (by means of a particular solvent used in a proper manner), the triglyceride of Wanklyn's aldi-palmitic acid, and another glyceride containing a new fatty acid with an iodine absorption considerably less than half that of oleic acid.

The whole results of my research in this direction will shortly be published, so in the meantime Mr. Allen will perhaps kindly explain the exact meaning of his most unaccountable and uncalled for criticism.—I am, &c.,

WILLIAM JOHNSTONE.

13, Fish Street Hill,
November 20, 1891.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxiii., No. 19, November 9, 1891.

Study of the Boron Phosphoiodides. — Henri Moissan.—Boron tri-iodide, BI_3, yields in the cold, in contact with a sulphocarbonic solution of phosphorus, a phosphoiodide of the formula PBI_2. This compound, which may be obtained in a crystalline state by volatilisation, yields when reduced in hydrogen the phosphoiodide PBI, and ultimately the phosphide PB. If it is still heated in hydrogen a part of the phosphorus escapes as a vapour, and there remains a new phosphide of the formula P_3B_5.

Existence of Acid or Basic Salts of the Monobasic Acids in very Dilute Liquids.—D. Berthelot.—

The author has shown that the addition of an excess of alkali to a neutral salt formed by the same alkali appears always to exert a slight chemical action, which is manifested only for the first portions of alkali, the succeeding portions having no particular effect. This phenomenon occurs as well with feeble organic acids, such as the acetic, as with the strong mineral acids. Hence it seems to result that even in very dilute liquids there is a tendency to the formation of a basic salt in small quantities, whilst the formation of an acid salt is less marked in solutions of the same dilution.

The Formation of Saline Hydrates at High Temperatures.—G. Rousseau.—The author's results seem to establish the formation of saline hydrates at high temperatures. He believes that it is possible to add new members to this family of compounds. Except manganese all the metals capable of giving rise to these hydrates belong to the eighth group of the periodic classification. From analogy it is legitimate to admit that the other members of this group may yield hydrates of the same order. The author purposes verifying this conjecture for the aurates and the osmites. Ruthenium, which was formerly placed in the eighth group, should be transferred to the seventh, following manganese according to the modified atomic weight assigned to it by the determinations of Joly. But the parallelism of the oxides of manganese and ruthenium enables us to foresee the existence of hydrated sodium and potassium ruthenites comparable to the alkaline manganites.

A Double Copper and Lithium Chloride.—A. Chassevant.—The author assigns to this compound the formula $2CuCl,LCl+5HO$. The salt does not dissolve in water without decomposition. If we add to it small quantities of water we obtain a green solution which quickly becomes blue. This colouration indicates the dissociation of the double salt in contact with water; the copper chloride and the lithium chloride are separated in the liquid. If we take as solvent a concentrated solution of lithium chloride the double chloride dissolves in it without decomposition, giving a reddish brown solution from which it can be re-crystallised.

Researches on Digitaleine.—J. Houdan.—The composition of digitaleine is $C_{62}H_{52}O_{24}$. Its most characteristic property is the following :—If we add amylic alcohol to an aqueous solution of digitaleine there is rapidly produced an abundant crystallisation. Digitaleine crystallised in ordinary alcohol loses its water and its alcohol at 110°. It dissolves slowly in cold water, but rapidly in boiling water. In absolute alcohol it is very sparingly soluble. Chloroform, ether, and ligroine only take up traces. It deflects the plane of polarisation to the left. It dissolves in hydrochloric acid without becoming coloured, but if the solution is heated it turns to a reddish violet with a slight green fluorescence. Dilute acids split it up into two glucosides without liberation of glucose.

On the Isocinchonines.—E. Jungfleisch and E. Léger. —A question of priority as against Herr Heese.

Determination of Fatty Matter in Dairy Products. —Lezé and Allard.—(See p. 265).

Ptomaines Extracted from Urine in some Infectious Diseases.—A. B. Griffiths.—The author has isolated the ptomaine of scarlet fever, $C_5H_{12}NO_4$, a white crystalline substance soluble in water and having a feebly alkaline reaction. It forms a crystalline hydrochlorate and a chloroaurate. It gives a yellowish white precipitate with the phosphomolybdic acid, a white with the phosphotungstic, and a yellow with picric acid. The ptomaine of diphtheria, $C_{14}H_{17}N_2O_6$, is also white and crystalline. It gives a hydrochlorate and a chloraurate. It is precipitated of a yellow colour by tannic acid and picric acid, white by phosphomolybdic, and brown by Nessler's reagent. A very poisonous ptomaine was obtained from a patient suffering from congestion of the kidneys, the

parotid and submaxillary glands. Its composition is $C_6H_{13}N_3O_3$. This base is transformed into creatine, then into methylguanidine. These three ptomaines are not found in normal urine.

Journal fur Praktische Chemie.
New Series, Vol. xliv., Parts 16 and 17.

Action of Hydrazine Hydrate upon Monoketones and Orthodiketones.—Th. Curtius and K. Thun.— Hydrazine hydrate acts upon the ordinary monoketones in a two-fold manner. If the ketones are introduced into an excess of hydrazine hydrate there are formed secondary nonsymmetric hydrazines which are very unstable and easily pass even in the cold into the very stable form of the azines, whilst hydrazine is split off. The same azines are obtained in a direct manner if the calculated quantity of hydrazine hydrate is added to 2 mols. of ketone. The authors have caused hydrazine hydrate to react upon acetone, methylethylketone, methylpropylketone, methylhexylketone, diethylketone, and acetophenone. In diketones on the action of hydrazine hydrate the keto-oxygen atoms are successively replaced by the hydrazi-group $(N_2H_2)^{ii}$.

Action of Hydrazine Hydrate upon Isatine and the Phenols.—Th. Curtius and K. Thun.—Isatine in contact with hydrazine hydrate behaves similarly to the ortho-diketonen. Equimolecular mixtures of phenol or hydroquinone and hydrazine hydrate yield, even when heated in sealed tubes to 130°, only the diammonium salts of these bodies.

Action of Hydrazine Hydrate upon Benzophenone. —Th. Curtius and F. Rautenberg.—An account of diphenylmethylenhydrazine, its behaviour with acids, diphenylmethylenhydrazine hydrochlorate, the acetyl derivatives of diphenylmethylenhydrazine, the decomposition of bisdiphenylazimethylen on boiling with acids; the behaviour of diphenylmethylenhydrazine when heated alone or with diphenylmethylentetrazone, the action of halogens and haloid hydracids upon the tetrazo-compound, the action of aldehyds and ketones upon diphenylmethylenhydrazine, diphenylmethylenbenzolazine, diphenylmethylencinnamalazine; the behaviour of chloral with diphenylmethylenhydrazine, diphenyldimethylazimethylen, diphenylmethylcinnamalazimethylen; the reaction of diphenylmethylenhydrazine and methylpropylketone and bisdiphenylazimethylen.

Phenomena of Isomeration of the Non-Saturated Hydrocarbons.—(Part IV.)—Al. Faworsky.—Monosubstituted acetylenhydrocarbons react on heating with alcoholic alkali. The first membrane of the series of the monosubstituted hydrocarbons, allylen, combines under these conditions the elements of the alcohol, and yields ethylisopropenylether; its higher homologues undergo an isomeric transformation. Monosubstituted acetylenes with primary alkyl radicles are isomerised to bisubstituted acetylenes. The isomerisation is complete at 140°—170°. Monosubstituted acetylenes with secondary radicles under the influence of alcoholic alkali are isomerised to nonsymmetric bisubstituted allines. With tertiary radicles the monosubstituted acetylenes do not react if heated with alcoholic alkali.

Researches from the Laboratory of the University of Freiburg.—These consist of a memoir by P. Heermann and N. Teclu on the nitroderivatives of a-naphtholethylether.

Characterisation of Flame.—N. Teclu.—The experiments described and illustrated in six figures show that a coal-gas flame by the action of atmospheric oxygen can be split up into two flames, one of which continues quietly burning at its original place, whilst the other travels downwards.

Optical Determination of the Quantity of Albumen in Urine.—H. O. G. Ellinger.—Already inserted.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Thermo-Chemistry.—A correspondent wishes for information as to where he can find thermo-chemical facts of elements (metals) not thermo-chemically known before 1886.

Gold-Aluminium.—Can any of your readers give me any information respecting the gold-aluminium alloy ($AuAl_2$) discovered by Prof. Roberts-Austen, or tell me where such can be obtained ?—A.B.

MEETINGS FOR THE WEEK.

MONDAY, 30th.—Society of Arts, 8. "The Pigments and Vehicles of the Old Masters," by A. P Laurie, M.A.
WEDNESDAY, Dec. 2nd.—Society of Arts, 8. "Secondary Batteries," by G. H. Robertson, F.C.S.
THURSDAY, 3rd.—Chemical, 8. "Phosphor Oxide (Part II.)," by Prof. Thorpe, F.R.S., and A. E. Tutton. "On Frangulin," (Part II.), by Prof. Thorpe and Dr. A. K. Miller. "The Structure and Character of Flames," by A. Smithells and H. Tingle. "The Composition of Cooked Vegetables," by Miss K. I. Williams. "On the Occurrence of a Mydicatic Alkaloid in Lettuce," by T. S. Dymond. "On Some Metallic Hydrosulphides," by S. E. Linder and H. Picton. "On the Physical Constitution of some Solutions of Insoluble Sulphides," by Harold Picton. "Solution and Pseudo-Solution," by H. Picton and S. E. Linder. Ballot for the Election of Fellows.
FRIDAY, 4th.—Physical. "On a Permanent Magnetic Field," by Mr. W. Hibbert. "Note on the Production of Rotatory Currents," by Prof. Ayrton, F.R.S.

THE CHEMICAL NEWS.

Vol. LXIV., No. 1671.

VACUUM SPECTRO-PHOTOGRAPHY.*

By Prof. V. SCHUMANN.

By means of a new vacuum spectro-photograph which I have personally constructed during the last twelve months, I have found it possible to resolve into separate lines the region of the hydrogen spectrum discovered last year (see CHEMICAL NEWS, vol. lxii., p. 299, Dec. 29, 1890), situate beyond the wave-length 1820, and, in addition, to photograph a more refrangible region which likewise displays a considerable wealth of rays. The number of the lines of the resolved groups is far greater than could be expected from my last year's photograms. For instance, in one of these groups, the length of which does not exceed 11 m.m., I count more than 90 sharply defined lines. The width of my slit had to be selected not above 0·004 m.m. The success of such delicate proofs depend also on an exceptionally fine texture of the sensitive plate.

NOTE ON ESTIMATION OF PHOSPHORIC ACID IN SLAGS.

By VINCENT EDWARDS, F.C.S.

HAVING to analyse some samples of slag which contained a considerable quantity of phosphoric acid, and finding they obstinately resisted treatment with aqua regia, it occurred to me that boiling with concentrated sulphuric acid might be effectual. This I carried out in a small flask, such as is used for Kjeldahl's process, adding a globule of mercury at the same time. I took about 0·5 grm. of the substance, which contained much silica and carbon, and boiled till almost white; this took a little over an hour. On cooling I diluted to 250 c.c., filtered off 100 c.c., and precipitated the P_2O_5 by direct addition of citro-magnesic solution and ammonia; after standing collected the precipitate, dissolved in dilute nitric acid, and estimated by uranium solution, it being impossible to weigh as the precipitate contained a white substance insoluble in nitric acid, most likely silica; this might, however, be removed by evaporation.

The process appears satisfactory, and gave 4·5 per cent P_2O_5 more than by treatment in the usual way with HCl and HNO_3. It is quite as simple as by any fusion method, and appears to be a means by which many complex substances which contain phosphoric acid might be dissolved and determined.

Lawes' Chemical Works, Barking,
November 12, 1891.

ON CHEMISM IN LIVING PROTOPLASM.

By Prof. W. PREYER and G. WENDT (of Berlin).

SINCE the memorable synthesis of urea, by which Woehler in 1828 gave a new direction to bio-chemistry, so many complicated products of animal and vegetable metabolism,—from formic acid to alizarine, salicine, coniine, and neurine,—have been obtained artificially, the somewhat premature conclusion that the belief in an especial vital force had been rendered perfectly untenable

* Extracts from a Letter from the Author to W. Crookes.

has constantly gained more adherents. The opponent of vitalism inferred that in living organisms the same powers must exclusively prevail as in inorganic nature, seeing that a series of chemical compounds, hitherto known only as the products of vital processes, had now been obtained in the laboratory.

Important as this assumption has been and will doubtless remain, it derives little support from synthetic chemistry. For however many products of the anaplastic or —which is less surprising—of the kataplastic metabolism of animals and plants are artificially put together from their elements by all manner of round-about methods, this is merely a fresh proof that these substances may be obtained by another process besides the one which the vegetal or animal organism uses in their production.

It is a fact that the chemist in his syntheses conducts a totally different process from the organism. Why, therefore, may not an especial energy be exerted in the organism, the so-called vital force? This question is raised by many to-day as it was sixty years ago. Quite recently at the opening of the British Association in Manchester, Roscoe said, after a decided rejection of the vitalistic hypothesis:—" We might raise the question whether any limit has been set to this synthetic power of the chemist? . . . Though the danger of dogmatising on the progress of science has already been seen in too many cases, we cannot help feeling that the chemist has for the present no prospect of breaking down the barrier which exists between the organised and the non-organised world."

Chemistry, as such without calling other facts into play, has certainly hitherto banished an especial vital power into the realm of fable. But if it should happen—and its early occurrence is important—it must be demonstrated that the chemical processes in the vegetal and animal organism must be capable of explanation by the existing natural laws, or by them and possibly by natural laws yet to be discovered and in harmony with them, and that in consequence some of the peculiar physiological reactions and syntheses can be elicited outside of the living organism exactly as within it.

This problem is capable of solution. But we must first apprehend what belongs to the performance of the ordinary chemical reaction; then which of these conditions are wanting or are modified in the chemical transformations in the organism, or if any novel conditions appear. If these differences are clearly shown, then such modified conditions for a chemical reaction can be produced artificially at pleasure; hence there would arise a bio-chemistry very different from and far more manifold than the chemistry of the day.

It may here be premised that such modified conditions of reaction really exist in the living cell, and that even in chemical manufactures " organism-reactions," accidentally discovered in practice, find their application. In such cases modern chemistry, when questioned concerning their origin, is accustomed to content itself with the phrase,—" not perfectly explicable."

A considerable number of misty conceptions, such as " katalysis," " power of contact," " ferment," " allotropy," &c., cannot hide the imperfections of such poor attempts at explanation, as they are recognised by every competent and reflective observer.

For a chemical reaction to take place a relatively considerable number of conditions must be fulfilled. To ascertain these we ask what occurs without exception in *every* chemical reaction; we then exclude strictly whatever is not to be observed in *every* case.

We then observe that whatever can always be shown in every chemical reaction is indispensable for the occurrence of such reaction, or is a necessary concomitant phenomenon.

Those natural processes which we call chemical reactions must be distinguished from all others by something in a genetic respect, which characterises them as chemical processes, and which must not be wanting if they are to

retain this character. This something must be that which always belongs to *all* chemical reactions.

Now it is a common character of all chemical reactions in the customary sense of the word occurring on the earth's surface that :—

1. Different materials come in direct contact.
2. Water or some other solvent must be present.
3. There arise electric currents.
4. Changes of volume and of
5. Thermic energy occur.
6. An action of mass is present.

In the text-books the chemical reaction, the foundation of chemistry, as such is scantily or not at all discussed. The metaphysical enquiry as to the ultimate ground throws the more proximate question into the shade. The six unconditional requirements of all chemical reactions are here collated probably for the first time.

It must be asked whether they are always to be found accompanying the chemism of organised matter. As the three fundamental functions of protoplasm, that ground-floor of all telluric life, we recognise :—(*a*) Change of matter ; (*b*) change of energy ; (*c*) change of form : *b* and *c* are impossible without *a*, and *a* consists of assimilation and dissimilation.

(To be continued).

THE BEHAVIOUR OF AZOIMIDE WITH LIVING ORGANISMS.*

By O. LOEW.

NITROHYDRIC acid or azoimide,—

$$\begin{matrix} N \\ \parallel \\ N \end{matrix} \Big\rangle NH,$$
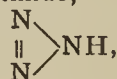
discovered by Th. Curtius in the past year, and made known by his laborious and dangerous researches, is not merely of profound chemical importance, but excites a physiological interest. Can the salts of this remarkable acid, like the nitrates and nitriles, serve as a source of nitrogen for the nutriment of vegetable cells ? If not, are these salts indifferent or poisonous ? If poisonous, wherefore ?

Having been put in possession of some sodium-azoimide by the great kindness of Prof. Curtius, I resolved to take these questions in hand.

1. *Experiments with Phanerogams.*

A culture solution was made up with magnesium sulphate and potassium monophosphate, 0·2 per thousand each ; potassium chloride and calcium chloride, 0·1 per thousand each ; and a trace of ferrous sulphate. To this liquid there was added 0·2 per thousand of sodium-azoimide ; and to a second portion, instead of the last-mentioned substance, an equal quantity of ammonium sulphate. In each solution there were placed three barley seedlings of 3 to 3·5 c.m. in length. The next day a great difference was visible ; the ammonia plants had grown distinctly, and measured on the third day respectively 10, 10·3, and 10·7 c.m. The azoimide plants had scarcely grown at all, and measured 3·1, 3·6, and 3·9 c.m. In the length of the roots there appeared an equally striking difference. On the fourth day yellow spots appeared on the leaves of the azoimide plants ; and on the fifth day from the commencement of the experiment the plants had faded, and were dying in all parts. The ammonia plants meantime developed in the normal manner. Even three seedlings which had been placed for comparison in well-water, without the addition of any nutrient salts, remained healthy, and grew for some time. Hence sodium azoimide had evidently exerted a poisonous action. A poisonous action was also observed in lupin

* *Ber. Deutsch. Chem. Gesell.*

seedlings, as the growth of the roots came to a close after the first day.

Leaves of *Valisneria spiralis*, after remaining for three days in the above solution of azoimide salt, had lost their vital turgescence, displayed no plasmatic currents, and the cells were dead. In the check solution, which contained nitrogen in the form of ammonium sulphate, the leaves remained alive and the cells displayed lively plasmatic currents. Leaves of the hazel-nut plant, placed in the solution of sodium-azoamide, showed brown spots after three days.

2. *Experiments on Algæ.*

A number of threads of *Spirogyna, Zygnema, Meso-carpus, Oscillaria*, also cells of Desmidiaceæ (*Closterium, Cosmarium*, various diatoms (*Nasicula, Gomphonema, Odontidium*), were placed in well-water containing 1 part per thousand of sodium-azoimide. After eighteen hours not the slightest injurious action could be detected under a magnifying power of 800 diameters. Not until the third day could a slowly progressive fading be detected. Even after ten days living cells could still be detected in the Algæ. The dead cells of the *Spirogyræ* showed a strong granulation of such an appearance as may be observed in the influence of ammonium salts at 1 part per thousand.

In the diatoms and *Oscillaria* the phenomena of movement did not totally disappear before the fifth day. At the same time the death of the protoplasm of the Desmidiaceæ was recognised.

If the above solution was diluted ten times, and mineral nutrient salts were added (0·1 of each per thousand), the Algæ above named remained living even after three weeks, and were healthy. Filaments of *Vaucheria* exhibited distinct growth.

Very different is the behaviour of the same Algæ with hydroxylamine and diamide. By these substances, at the same dilution (0·1 per thousand), the Algæ are killed within forty-eight hours at furthest, even in a perfectly neutral solution.

3. *Experiments with Bacteria.*

One portion of a culture solution of the following composition — Potassium sodium tartrate, 1 per cent ; potassium diphosphate, 0·1 per cent ; magnesium sulphate, 0·05 per cent ; calcium chloride, 0·05 per cent—was mixed with 0·1 per cent sodium azoimide, a second with 0·1 per cent diammonium phosphate, and a third with both these nitrogen compounds together. The three mixtures were then infected with bacteria which had grown in a methylic nutrient solution on exposure to the air. After forty-eight hours the second portion showed a strong bacterial turbidity, whilst the microscope showed a vast quantity of bacteria, which quickly effected the fermentation and combustion of the tartaric acid in the nutrient solution. The two others, even after standing for six weeks, and after repeated infection, remained perfectly clear, and developed not a trace of bacteria. Even when the solutions were diluted fivefold, and infected afresh, there were still no living bacteria. They were thus again diluted twofold, so that they only contained 0·1 per thousand sodium azoimide ; 0·5 per cent glucose was added. They were infected again, and let stand for fourteen days in an open flask. No bacterial turbidity appeared, but a few living bacteria were present. That flask which contained ammonia along with the sodium-azoimide displayed a thin film of *Saccharomycetes* (probably *S. ellipsoideus*).

(To be continued.)

A Treatise on Manures.—Messrs. Whittaker and Co. have in the press a second edition of Dr. A. B. Griffiths's " Treatise on Manures." It is a little more than two years since the work appeared ; therefore, to bring the new edition up to date, it has been necessary to add fifty pages of new matter.

DETERMINATION OF SMALL QUANTITIES OF ALKALI AND RECOGNITION OF THE NEUTRALITY OF WATER.

By F. MYLIUS and F. FOERSTER.

(Continued from p. 266).

AFTER a few minutes it is allowed to flow into a second similar parting funnel, where it is shaken with 10 c.c. of aqueous ether in order to remove again the greatest part of the free eosine taken up by the water at the first shaking. The solution thus twice shaken is lastly collected in a flask in order to compare it with a solution of alkaline eosinate of known strength. Such a comparative solution is made up with a number of c.c. of the above-named alkaline solution of iodeosine diluted with water. For comparison solutions are preferred the colouration of which corresponds to 5—20 c.c. of the original solution in 100 c.c. and strata of liquid of 5—15 c.m. in depth. On account of the small extent of these figures, it is often necessary to dilute the coloured solution in a suitable manner. Here, and in measuring out the comparative solution, it must be remembered that the quantity of liquid used for comparison = 110 c.c. For the purpose of comparison, Wolff's colorimeter is very suitable, in which the adjustment of two solutions for equality of colour is effected by regulating the depth of the strata.

As regards the calculation of the determinations which have been carried out by the above-named process, it was already mentioned that we cannot conclude directly the quantity of alkali present from the red colouration of the shaken solution by comparison with a solution of sodium eosinate of known strength and of an equal intensity of colour. Into the watery stratum there passes, as already mentioned, some free eosine, which partly remains there after the second shaking; this introduction is, however, exceeded by the eosine given off to the ether in consequence of the hydrolytic fusion of the alkaline eosinates. Both these influences cannot be calculated, and hence it becomes necessary to multiply the quantity of alkali calculated directly from the red colouration observed by an empirical factor in order to obtain the quantity of alkali really present. In order to find such a factor there were carried out a series of determinations with varying quantities of a solution of soda containing 1·0 m.grm. Na_2O per litre. It appeared that on employing every precaution required by the sensitiveness of the method, equal results were obtained under like conditions, though, as it might be expected, the values found show deviations which may amount to 10 per cent of the total. The following table contains the mean values from a series of separate determinations :—

Quantities of Na_2O employed in thousandth m.grms. in 100 c.m.	Colour observed corresponds to c.c. of eosine solution.	Thousandth m.grm. Na_2O would correspond to the colouration.
0	5·6	—
10	14·5	6·6
15	20·5	11·0
20	25	14·3
25	31	18·8
40	45	29·1
60	60	44·7
80	86	59·5
100	104	72·8

From the above it will be seen that the increase of the red colouration observed corresponds approximately with the quantities of alkali present. In the third column those quantities of alkali are laid down which must be present if all the alkali is present as neutral sodium eosinate; therefore it 1 c.c. of the eosine solution corresponds to the equivalent quantity of soda, *i.e.*, 0·00074 m.grm. Na_2O, the number of the c.c. taken into calculation is that observed with deduction of the 5·6 c.c. eosine

solution required by pure water, as this difference can only be referred to the alkali present. It is observed that the quantities of alkali computed in this manner approximate very closely to the same fraction of that really present, *i.e.*, on the average 72·4. In order to raise this 72·4 to 100 it must be multiplied with $100/72·4 = 1·38$.

Hence 1 c.c. of the alkaline solution of eosine represents—

0·00102 m.grm.		Na_2O.
0·00154	,,	K_2O.
0·00056	,,	NH_3.
0·00189	,,	CaO.

An example will explain what has been said. In the above conspectus we find that the colour observed corresponds to 45 c.c. of the eosine solution; as the "eosine value" of pure water = 5·6, the colour corresponding to the alkali = 39·4 c.c. solution of eosine. If all the alkali were present as neutral sodium eosinate, 1 c.c. of eosine solution would = 0·00074 m.grm. Na_2O; but in fact 1 c.c. corresponds to 1·38 times this quantity of alkali; that is, to 0·00102 m.grm. Na_2O. Hence 39·4 c.c. correspond to 0·0402 m.grm. Na_2O, and the quantity employed would be 0·0400 m.grm. Na_2O.

How far we arrive at an agreement between the quantities of alkali used and detected will be seen from the following conspectus :—

Potassa.

Used.	Foun
15·16	14·2
30·32	32·1
60·64	58·9
90·96	88·3
151·6	160·1

Ammonia.

Used.	Found.
10·96	11·4
21·92	20·4
54·84	55·4

(To be continued.)

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING OCTOBER 31ST, 1891.

By WILLIAM CROOKES, F.R.S.;

WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford ;

and C. MEYMOTT TIDY, M.B., F.C.S., Barrister-at-Law,
Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, Metropolis Water Act, 1871.

London, November 7th, 1891.

SIR,—We submit herewith the results of our analyses of the 189 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from October 1st to October 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 189 samples examined, all were found to be clear, bright, and efficiently filtered.

As a consequence of the exceptionally flooded state of the rivers during the greater portion of the month of October, the character of the water supplied to the Metropolis, in respect to its degree of freedom from organic matter, was on the whole less satisfactory than it has been found for a long time past. The New River Company's supply, though appreciably affected towards the end of the month, maintained a high average standard; while the supply of the East London Company from the Lea, and that of the Chelsea Company from the Thames, were, owing doubtless to the large storage area of these two Companies, not affected by the floods to any notable extent. In the case of the other Thames-supply Companies, in different degrees in different instances, the proportions of organic matter present, as indicated by the degree of colour-tint of the water, and estimated by the combustion and oxidation processes, were appreciably in excess of the proportions habitually met with. The mean proportion of organic carbon present in the Thames-derived supply was 0·197 in 100,000 parts of the water, as against a mean of 0·129 part in the previous month's supply; while, in two samples, the maximum amounts were found to be 0·395 and 0·422 part respectively,—the variation of amount in the other samples examined ranging from 0·143 part to 0·241 part in 100,000 parts of the water.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
WILLIAM ODLING.
C. MEYMOTT TIDY.

OCCURRENCE OF A NATURAL SULPHIDE OF GOLD.

By T. W. T. ATHERTON.

THE existence of gold in the form of a natural sulphide in conjunction with pyrites has often been advanced theoretically as a possible occurrence, but up to the present time this occurrence has, I believe, never been established as an actual fact.

During my investigations on the ore of the Deep Creek Mines, I have found in them what I believe to be gold existing as a natural sulphide. The description of this ore will, no doubt, be of interest to your readers.

The lode is a large irregular one of pure arsenical pyrites, existing in a felsite dyke near the sea coast. Surrounding it on all sides are micacious schists, and in the neighbourhood is a large hill of granite about 800 feet high. In the lode and the rock immediately adjoining it are large quantities of pyrophyllite, and in some places of the mine are deposits of this pure white, translucent mineral, but in the ore itself it is a yellow and pale olive-green colour, and is never absent from the pyrites.

From the first I was much struck with the exceedingly fine state of division in which the gold existed in the ore. After roasting and very carefully grinding down in an agate mortar, I have never been able to get any pieces of gold exceeding the one-thousandth of an inch in diameter, and the greater quantity is very much finer than this. Careful dissolving of the pyrites and gangue, so as to leave the gold intact, failed to find it in any larger diameter. As this was a very unusual experience in investigations on many other kinds of pyrites, I was led further into the matter. Ultimately, after a number of experiments, there was nothing left but to test for gold as a sulphide.

Taking 200 grms. of pyrites from a sample assaying 17 ozs. fine gold per ton, grinding it finely, and heating for some hours with a solution of sodium sulphide (Na_2S_2), on decomposing the filtrate and treating it for gold I got

a result at the rate of 12 ozs. gold per ton. This was repeated several times with the same result.

This sample came from the lode at the 140 feet level, whilst samples from the higher levels where the ore is more oxidised, although carrying the gold in the same degree of fineness, do not give as high a percentage of auric sulphide.

It would appear that all the gold in the pyrites (and I have never found any apart from it), has originally taken its place there as a sulphide.

The following is an analysis of a general sample of the ore :—

				Per Ton.
Silica ..	..	13·940	p.c.	
Alumina	..	6·592	,,	
Lime ..	..	0·9025	,,	
Sulphur .	..	16·584	,,	
Arsenic .	..	33·267	,,	
Iron ..	..	27·720	,,	
Cobalt ..	..	0·964	,,	
Nickel ..	..		Traces	
Gold ..	..		5 ozs. 3 dwts. 8 grs.	
Silver ..	..		0 ,, 16 ,, 0 ,,	

99·969

Nambucca Head's Gold Mining Company,
Deep Creek, N.S. Wales, Oct. 9, 1891.

PROPERTIES OF PRECIPITATES, &c.*

By E. WALLER, Ph.D.

(Concluded from p. 269).

SnS_2.

Rem.—Usually precipitated by H_2S in acid solution, or by acidifying solutions of alkaline sulpho-stannate. Obtained for purposes of separation, or for determination as SnO_2 after oxidising. Disposition to run through the filter checked by alkaline acetates or nitrates, &c.

Cond.—Solution slightly acid, moderately dilute. Precipitation promoted by acetates, interfered with by alkaline oxalates or oxalic acid.

Sol.—Moderately concentrated acid, especially HCl, dissolve or prevent precipitation. The influence is more marked the more concentrated the acid, or the higher the temperature. Soluble in a boiling solution containing free $H_2C_2O_4$. (Separation from Sb.)

Ign.—If rapidly and strongly heated, some SnS_2 may be volatilised. By moderate heating with access of air, SnO_2 forms without loss. It is, however, usual to assist the oxidation with a few drops of HNO_3 added from time to time.

Ammonium Phosphomolybdate. $12MoO_3(NH_4)_3PO_4+$.

Rem.—Yellow, finely-crystalline precipitate. Precipitant $(NH_4)_2MoO_4$ in HNO_3 solution. The ratio of MoO_3 to P_2O_5 in the precipitate varies according to the proportion of substances present in the solution (NH_4NO_3, $Fe_2(NO_3)_6$, &c.), the proportion of free acid, the kind of acid, the length of time elapsing before filtering, and the temperature at which it is effected. With the same or closely similar conditions, the ratio of MoO_3 to P_2O_5 is essentially the same. Precipitation promoted by agitation. When precipitation is complete, the precipitate settles rapidly after stirring. Precipitated under the conditions described by Emmerton (volumetric determination of P in irons), the ratio of MoO_3 to P_2O_5 is 24 to 1.

Cond.—Solution should be acid with HNO_3. Too much free HNO_3 retards, or may prevent complete precipitation; too little allows Fe_2O_3 to come down with it, in which case the colour is more orange. An excess of the

* From *School of Mines Quarterly*, xii., No. 4.

precipitant should be present; also at least 10 grms. of NH_4NO_3 for every 0·1 grm. or less of P present. Temperature should be 70—85° C. Below 70° the separation is very slow, whereas on boiling (other conditions being right), MoO_3 or Fe_2O_3 may accompany the precipitate. Reducing agents, organic acids, silica, chlorides, and HCl, should be absent. H_2SO_4 and sulphates retard precipitation. If the precipitate is to be dissolved for volumetric estimation, in a solution of material containing but little iron, some iron should be added to give correct results, or the standard should be obtained with material of the same character.

Sol.—Readily dissolved by NH_4OH and other alkalies; also by alkaline phosphates. If the ammonia is too strong, however, the solution will be turbid with $(NH_4)_2MoO_4$. Dissolved or decomposed by water alone, the more readily the higher the temperature. Precipitation prevented by tartaric acid or organic substances of that class. Somewhat soluble in HCl, or moderately strong H_2SO_4 and HNO_3. Insoluble in weakly acid solutions and acid solutions of NH_4 salts. Solution for washing should contain 1 per cent HNO_3 and 10 per cent NH_4NO_3, or a corresponding amount of H_2SO_4 and $(NH_4)_2SO_4$.

Contam.—Arsenio-molybdate, silica, Fe_2O_3, TiO_2.

Arsenio-molybdate precipitates the less readily the lower the temperature. By allowing the solution to stand for about two days at 40° C., the phospho-molybdate may be precipitated free from arsenic. When present, however, As is separated either before or after.

Silica, either as hydrated SiO_2 or as silico-molybdate (the existence of which is disputed), may be present. By allowing the ammonia solution to stand for some time after addition of NH_4Cl, the flocculent silica separates and may be filtered off.

Fe_2O_3 in the precipitate often causes it to separate in crusts on the sides of the beaker. On attempting to dissolve in ammonia, yellow to red $Fe_2(OH)_6$ mixed with $Fe_2(PO)_2$ remains undissolved. After washing with ammonia this residue is dissolved in HNO_3, the solutions united and re-precipitation effected, after acidifying with HNO_3.

Hydrated TiO_2 (which retains P_2O_5) can be separated by fusing the portion insoluble in ammonia for some time with Na_2CO_3 (*vide* Na_2TiO_3), leaching with water, and in the water solution re-precipitating with the molybdate reagent.

SILICA.

Rem. and Cond.—On adding an excess of mineral acid to a solution containing a silicate, free silicic acid containing indefinite amounts of water is formed, partially or entirely soluble. On evaporation H_2O (of constitution) is removed and insoluble SiO_2 is separated, which may be filtered off after digestion with diluted acid. HCl is the acid most frequently used. When HNO_3 is used, regard must be had to the fact that certain nitrates ($Fe_2(NO_3)_6$, &c.), are decomposed at the temperature usually employed to drive out the last portions of the water (110—130° C.), and are not readily re-formed by digestion with diluted HNO_3. The heat is usually maintained until there is no perceptible odour of acid. With H_2SO_4, the heat is continued until fumes of SO_3 are evolved, indicating that H_2SO_4 is the only free acid remaining. If the heat has not been sufficiently prolonged or intense, the separated silica may be flocculent and filters with difficulty, or some may remain soluble.

If the heat has been too high, the conditions may have favoured a re-combination of silica with the bases, and consequent soluble silica (analogous to the action by fusion). The temperature which can safely be applied may be put at 110—120°.

According to Gilbert (*Technical Quarterly*, February, 1890), when only Ca and alkalies are present, the temperature of drying may be carried up to 280° C. without detriment; but if Mg is present, re-combination of the

bases with the silica is best prevented by drying at 120° C. Some alumina almost invariably remains with the silica if Al is present in the solution.

Sol.—Dissolved by boiling or fusing with fixed alkalies, caustic or carbonated. Insoluble in water and acids (HFl excepted).

Contam.—Insoluble sulphates ($PbSO_4$, $BaSO_4$) removed by digestion with concentrated H_2SO_4, and filtering through asbestos. (For other solvents of these substances, *vide* sup.) In some cases $CaSO_4$, removable by digestion with HCl and NH_4Cl. The precipitate may also contain a form of $Fe_2(SO_4)_3$ (when separated from concentrated H_2SO_4) which dissolves in dilute H_2SO_4 with some difficulty, but is readily soluble in HCl.

SnO_2 or Sb_2O_4 may be retained, as well as TiO_2 (possibly combined with P_2O_5) and ferric or aluminic oxides or basic salts. TiO_2 tends to hold P_2O_5, Al_2O_3 and Fe_2O_3 in the precipitate. To avoid error in such cases the SiO_2 should be determined by loss, adding HF or NH_4F (and in any case H_2SO_4), igniting off SiF_4, and weighing again. This treatment is advisable whenever Al_2O_3 is present in the solution in any quantity.

Ign.—Precipitate is very light and fine, and readily carried off by flame, requiring especial precaution on igniting. After ignition, the precipitate will absorb appreciable amounts of water if exposed to air containing moisture.

ON THE OCCURRENCE OF NITROGEN IN URANINITE, AND ON THE COMPOSITION OF URANINITE IN GENERAL.*

By W. F. HILLEBRAND.

(Continued from p. 257.)

TABLE III.—*Uraninite from Colorado and North Carolina.*

	IX. Colorado.			X. North Carolina.	XI. North Carolina.
	a.	*b.*	Mean.		
UO_3	25·26	—	25·26	50·83	44·11
UO_2	58·47	58·56	58·51	39·31	46·56
TiO_2	trace	trace	trace	—	—
ZrO_2	7·32	7·85	7·59	—	—
ThO_2	—	—	—	2·78	
CeO_2	0·22	0·22	(*a*)0·22	0·26	
$(LaDi)_2O_3$	—	—	—	0·50	3·04
$(YEr)_2O_3$	—	—	—	0·20	
PbO	0·69	0·71	0·70	4 20	4·53
ZnO	0·43	0·44	0·44	—	—
FeO	0·32	—	(*b*)0·32	trace	—
MnO	0·16	—	0·16	—	—
CaO	0·84	0·85	0·84	0·85	0·23
MgO	trace?	—	trace?	0·30	0·25
Alk	trace?	—	trace?		
H_2O	1·96	—	1·96	1·21	undet.
N	0·15	—	(*c*)0·15	(*d*)0·37	undet.
SiO_2	2·76	2·82	2·79	0·08	0·13
P_2O_5	0·22	—	0·22	?	—
As_2O_5	0·43	—	0·43	—	—
$CuFeS_2$	0·12	—	0·12	—	—
FeS_2	0·24	—	0·24	—	—
Insol.	—	—	—	0·10	0·06
Total	—	—	99·95	100·99	98·91
All U as UO_2	—	—	82·36	87·31	88·21
Sp. gr.	—	—	8·068	8·086	9·492
Temp., °C.	—	—	20	15·8	20

* From "Bulletin No. 78, U.S. Geological Survey, 1889—90." An abstract of this paper was published in the *Am. Jour. Sci.*, vol. xl., p. 384.

TABLE IV.a.—*Uraninite from Norway.*

	XII. Anneröd. a.	b.	XIII. Elvestad. a.	b.	XIV. Elvestad. a.	b.	XV. Skraatorp. a.	b.	XVI. Huggenäskilen. a.	b.	XVII. Arendal.(h)	XVIII. Arendal.
UO_3	30·56	30·70	25·34	{25·49 / 25·26}	22·02	22·06	31·93	32·08	35·52	35·57	41·71	26·80
UO_2	46·20	46·07	50·76	{50·62 / 50·84}	43·05	43·01	43·95	43·81	43·36	43·39	24·18	44·18
ZrO_2	0·06	—	0·08	—	—		—	—	—	—	—	—
ThO_2	6·00	—	8·48	—			8·98	—	6·59			4·15
CeO_2	0·18	—	0·21	—	8·43		0·17	—	0·20	8·13	3·66	none
$(DiLa)_2O_3$	0·27	—	0·26	—			(f)0·36	—	0·23			(i)0·67
$(YEr)_2O_3$	1·11	—	(c)1·10	—			0·97	—	1·03		9·76	9·05
PbO	9·04	—	10·06	—	8·58	8·58	9·50	9·42	9·46	{9·45 / 9·41}	10·54	10·95
CaO	0·37	—	0·77	—	0·37	—	0·36	—	0·41	0·41	1·06	0·61
MgO	} trace	—	trace	—	0·13	—	trace	—	0·13	—	{ 0·10	0·04
Alk											0·23	0·15
H_2O	0·74	—	0·73	—	0·74	—	0·77	—	0·79	—	1·23	undet.
N	1·18	(b)1·15	1·28	(d)1·29	1·08	—	1·03	—	1·08	—	undet.	1·24
Fe_2O_3	0·25	—	0·21	—	0·30	0·31	0·09	—	0·32	0·31	0·03	0·24
MnO	—	—	0·06	—	—	—	—	—	—	—	—	—
SiO_2	0·22	—	0·38	0·39	0·28	0·30	0·53	—	0·45	{0·51 / 0·50}	0·90	0·50
P_2O_5	0·02	—	0·04	—	trace	—	(?)	—	trace	—	—	trace
Insol...	(a)4·42	—	0·44	0·46	(e)15·50	15·41	(g)1·54	—	0·41	0·43	1·10	1·19
All U as UO_2	75·06	—	74·69	—	63·84	—	74·10	—	76·90	76·98	63·57	69·49

(a) The gangue was mainly columbite, and contained a total of 61 FeO by trial on a separate portion. The columbite could be pretty well separated from the other and lighter gangue matter after solution of the uraninite in nitric acid, and it was found that of the total FeO, 0·30 belonged to the columbite and 0·31 to the other gangue constituent. This latter was dissolved by the acid in UO_2 determinations, while the columbite was not; hence a correction has been made for 0·31 FeO representing 0·58 UO_2.

(b) The first result by fusion with $NaKCO_3$, the second by solution in HCl. Another result of 1·28 by H_2SO_4 was the first quantitative determination of nitrogen made, and was probably too high through leakage of air into the receiver.

(c) Molecular weight, 277.

(d) By fusion with $NaKCO_3$. The first result was obtained by H_2SO_4.

(e) Almost entirely columbite.

(f) Perhaps not fully freed from THO_2.

(g) Mainly a phosphate.

(h) A brief but brisk effervescence was produced by acids. The deficiency in the analysis, 5·50 per cent, was supposed to be satisfactorily accounted for as CO_2; a portion of it, however, is probably to be credited to nitrogen.

(i) The ignited oxides differed in appearance from the mixtures of La_2O_3 and Di_2O_3 obtained in all other analyses, being nearly colourless.

TABLE IV.b.—*Means of Analyses in Table IV.a.*

	XII. Anneröd.	XIII. Elvestad.	XIV. Elvestad.	XV. Skraatorp.	XVI. Huggenäskilen.	XVII. Arendal.	XVIII. Arendal.
UO_3	30·63	25·36	22·04	32·00	35·54	41·71	26·80
UO_2	46·13	50·74	43·03	43·88	43·38	24·18	44·18
ZrO_2?	0·06	0·08		—	—		—
ThO_2	6·00	8·48		8·98	6·63		4·15
CeO_2	0·18	0·21	8·43	0·17	0·20	3·66	none
$(DiLa)_2O_3$	0·27	0·26		0·36	0·23		0·67
$(YEr)_2O_3$	1·11	1·10		0·97	1·03	9·76	9·05
PbO	9·04	10·06	8·58	9·46	9·44	10·54	10·95
CaO	0·37	0·77	0·37	0·36	0·41	1·06	0·61
MgO	} trace	trace	0·13	trace	0·13	{ 0·10	0·04
Alk						0·23	0·15
H_2O	0·74	0·73	0·74	0·77	0·79	1·23	undet.
N	1·17	1·28	1·08	1·03	1·08	undet.	1·24
Fe_2O_3	0·25	0·21	0·30	0·09	0·32	0·03	0·24
MnO	—	0·06	—	—	—	—	—
SiO_2	0·22	0·38	0·29	0·53	0·49	0·90	0·50
P_2O_5	0·02	0·04	trace	(?)	trace	—	trace
Insol...	4·42	0·45	15·45	1·54	0·42	1·10	1·19
Total	100·61	100·21	100·44	100·14	100·09	94·50	99·77
Sp. gr.	8·893	9·145	8·320	8·966	8·930	7 500	—
Temp. °C	21·6	17	29·7	20	28·2	26·8	—

Notes to Table III. p. 279.

(*a*) Lanthanum not tested for.

(*b*) Calculated from total iron after deducting that required by pyrite and chalcopyrite.

(*c*) By fusion with $NaKCO_3$. H_2SO_4 failed to decompose entirely in nine days at 100° C.

(*d*) Mean of 0·38 by fusion with $NaKCO_3$ and 0·35 by H_2SO_4.

IX. From a specimen in the National Museum from near Black Hawk, Colorado, where the mineral was originally identified by Mr. Richard Pearce about 1872. A very few tons represented the total product of the mine in uraninite, which was shipped to Great Britain for treatment.

This variety, differing in some respects so markedly in composition from all other known uraninites, is also distinguished from the other North American occurrences by its utter want of crystalline form. The specimen examined was largely contaminated with pyrite and chalcopyrite; in places it consisted of these alone, in others of pretty pure uraninite. But the purest of the latter was seamed with minute cracks filled with sulphides. A section as thin as possible showed under the microscope absolutely no other impurity. The material used for analysis was obtained, after sifting to grades of fineness, by first panning and then exposing the partly cleaned grains in a specially devised apparatus to an upward current of water, through which the heavy uraninite fell while the sulphides were held up. It was then further purified by most laborious hand-picking under the lens. Even so it was impossible to free it altogether from sulphides, as the analysis shows, and this is especially unfortunate because of the uncertainty which is thereby thrown upon the UO_2 estimations. These, as above given, *include* the effect of any hydrogen sulphide and ferrous iron formed by the solvent action of sulphuric acid and of ferrous oxide possibly already existing. That they are not far from correct, however, is evidenced by a gravimetric estimation of UO_2 after separation by hydrofluoric acid, where sulphides and ferrous iron would be without effect, which gave 58·24 per cent UO_2. Another element of uncertainty in the volumetric determination is caused by want of knowledge of the condition in which arsenic is present. It has been assumed as As_2O_5, mainly for the reason that when even dilute nitric acid was used for dissolving, hydrogen sulphide precipitated the arsenic only after a considerable time. The condition of the zinc is likewise unknown. Its most natural form would be as sulphide; but as the sulphur was insufficient for the zinc alone, the negative element has all been credited to pyrite and chalcopyrite.

The analysis presented considerable difficulty. It was found that, on solution in nitric acid, a dirty white residue was left which contained silica, zirconia, and phosphoric acid, and that on boiling a further precipitate of zirconia containing phosphoric acid came out. None of the silica was present as quartz, for the residue in nitric acid was entirely free from grit; nor can it have been combined with zirconia as zircon, for the same reason and because the latter is insoluble. But for the phosphoric acid it is probable that the residue would have held no zirconia, since a very little of the former seems able to carry down much of the latter, even in a very acid solution. The silica given in the analysis represents both that in the residue and that subsequently obtained by evaporation after boiling and filtering. The rest of the zirconia and the other earths were separated from uranium by potassium sulphate.

X., XI. From the Flat Rock mine, Mitchell County, North Carolina, through Mr. W. E. Hidden. Entirely unaltered uraninite seems never to have been found in North Carolina, and no analysis of it appears to have been made, though its alteration products have received attention. The crystal form of the original mineral is often preserved in the pseudomorphs, and it is decidedly more cubical than that of the Connecticut crystals, which are usually octahedral in habit. Even the least-altered material, though it may present a perfectly fresh aspect, is seamed in all directions by microscopic cracks filled with yellow alteration products. Such was the character of the piece used for analysis X., which was undertaken for the purpose of ascertaining whether or not the North Carolina mineral contained rare earths. In order to observe the effect of a weak solvent another lump was immersed for several days in very dilute cold hydrochloric acid, whereby it gradually fell into a fine powder, which was washed, dried, and analysed with the results given under XI.

XII. The original bröggerite, from Gustavsgruben, Annerröd, near Moss, received from Prof. W. C. Brögger, who writes " Es ist das originale Vorkommen des Bröggerit Blomstrands."

XIII. Likewise from Prof. Brögger, labelled " Uraninit, Elvestad b. Moss." In addition Prof. Brögger writes, " So viel ich weiss, von derselben Stelle wie das Originalmaterial Lorenzens."

XIV. to XVIII. From Prof. A. E. Nordenskiöld, through Prof. F. W. Clarke, of the U.S. Geological Survey. These specimens all bore, with one exception erroneously as the analyses show, the name cleveite, on labels of the Royal Museum of Stockholm; XIV. was from Elvestad, XV. from Skraatorp, XVI. from Huggenäskilen, all being localities near Moss, and XVII. and XVIII. were from Arendal. The Arendal material was not in separate crystals and fragments like the others, but was inclosed in the original matrix of felspathic rock. Of this there were three or four small pieces, from one of which some very inferior-looking material was extracted. It had every appearance of being much altered, which the evolution of carbonic acid by acids and the abnormally low percentage of UO_2 seemed so fully to demonstrate that no particular pains were taken beyond separating the earths from uranium and dividing them roughly into two groups. The material was in any case insufficient for a carbonic acid estimation. Later it became of interest to learn if this apparently greatly altered material contained nitrogen, and to this end further material was extracted from another of the pieces of rock. Its analysis unexpectedly gave the results under XVIII., the water alone being undetermined for want of material.

(To be continued).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.
November 20th, 1891.

Prof. W. E. AYRTON, F.R.S., President, in the Chair.

DR. PHILIPPE A. GUYE gave a short account and discussion of the various forms which have been given to the general equation expressing the behaviour of liquids and gases under different conditions of volume, temperature, and pressure, by Van der Waals, Clausius, Sarran, Violi, Heilborn, and Tait. He first considered the equation of Van der Waals, which, although only an approximation to the true one, may be made to lead to numerous important deductions. He then showed that of the various more exact formulæ proposed, that of Sarran is the simplest, and may be used with less expenditure of time and trouble than any of the others. In conclusion he insisted on the necessity of experimental researches as the only means of arriving at a definite conclusion as to which of the various formulæ is the true one; such researches should involve determinations, as exact as

possible, of the critical constants, and of isotherms at high temperatures and great pressures.

Prof. RAMSAY inquired whether the constants in the formula of Clausius had any physical meaning or were they merely numbers?

M. GUYE, in reply, said that although *some* of the constants in the improved formulæ had physical interpretation Van der Waal's equation was the only one in which *all* the constants had precise physical significations.

Prof. RÜCKER said it was only necessary to look at the formulæ to see how important a factor Van der Waals' expression had been in later developments of the subject. Although it did not agree with experiment under all conditions, particularly at small volumes, yet it was a close approximation over a considerable range, and was the only formula in which all the constants had definite physical meanings. Prof. Tait had pointed out that the number of constants were too few to fully represent the facts, for by following Andrews' reasoning he had shown that about the critical point a straight line cuts the isotherm in five points. Nevertheless, during the last twenty years all the so-called improved formulæ were modifications of Van der Waals' expression, and this, he thought, showed how valuable the original formula was.

Prof. FITZGERALD said he once tried how far Clausius's formula agreed with the experimental results published by Messrs. Ramsay and Young, and after several months' work relinquished it on account of the tremendous labour involved. He thought that such complicated formulæ retarded rather than advanced science; simple ones (even if less accurate) were likely to lead to greater advancement.

Prof. CAREY FOSTER remarked that the expression $p v = RT$, which is nearly true for gases, was the starting-point of all subsequent advances. Van der Waals had arrived at a still closer approximation by taking into account the volume occupied by the particles and their mutual pressure.

The PRESIDENT said Van der Waals' memoir had been adversely criticised because of its supposed insufficient recognition of Andrews' investigations on the subject. Better acquaintance with the work had, however, shown this criticism to be undeserved.

Dr. C. V. BURTON read a paper on "*A New Theory concerning the Constitution of Matter.*" It is assumed that it is possible to have in the ether a distribution of strain which is itself in equilibrium. Such a distribution is called a "strain-figure." An atom is looked upon as an aggregation of strain-figures, the possible *varieties* of strain-figures (and hence of atoms) being limited by the conditions of equilibrium, and the *sizes* of possible strain-figures dependent on the coarse-grainedness of the turbulent motion or other structure of the ether.

The motion of matter is considered to be merely the transference of a strain distribution from one portion of the ether to another. This the author illustrated by causing a loop to travel along a rope, the loop being regarded as a strain-distribution, which is propagated along the rope whilst the rope itself is not transferred. Such transference may occur without encountering any resistance, and the strain-figure will retain the same form, provided the velocity is small compared with that at which gravitation is propagated.

The equations of motion of a strain-figure are deduced and are shown to be identical with those of ordinary matter, provided certain conditions of symmetry are realised.

It is also shown under what conditions an atom consisting of strain-figures would have a finite number of degrees of freedom, and some attempt is made to examine how gravitation and other attractions might follow from a distribution of stress in the strained ether. An inquiry is also made into the reason why elements have fixed properties, and their transmutation is discussed.

Prof. FITZGERALD, referring to the elastic solid theory of the ether, said Sir W. Thomson's more recent papers had thrown considerable doubt upon it. The propagation of strain-figures was, he thought, a case of wave motion. In his lectures he had likened the passage of matter through space to that of a drop of water through ice, the ice in front melting and the rear of the drop freezing as the liquid state progressed.

Many points raised in the paper were, he said, very interesting, and the suggestion that the discrete nature of atoms is the result of the coarse grainedness of matter, very good. On the other hand he considered the static treatment of strain-figures improper, for the ultimate conditions must be kinetic.

Dr. O. LODGE agreed with Prof. Fitzgerald in regarding the motion of the loop along the rope as a wave motion, whose velocity of propagation is equal to that of the loop. A similar case occurs when a ring of rope is spinning, and has a pulse impressed on it at one point, for the pulse travels at the same speed as the rope.

A paper on "*A Permanent Magnetic Field*," by Mr. W. HIBBERT, was postponed until next meeting.

CORRESPONDENCE.

THE SAPONIFICATION OF BEEF FAT.

To the Editor of the Chemical News.

SIR,—I observe (page 273) that Dr. Johnstone is still dissatisfied with my statement that he had recently published experiments (*Analyst*, xvi., 26) according to which beef fat requires 23 per cent of caustic potash for its saponification. As I pointed out in a previous letter, Dr. Johnstone's position is similar to that of a man who has stated that he was born in 1868, and then objects to others holding that his age is now twenty-three.

As Dr. Johnstone asks me to explain the exact meaning of my "most unaccountable and uncalled-for criticism," I have much pleasure in reminding him that chemists are in the habit of expressing the amount of alkali required to saponify a fat in terms of caustic potash (KHO), and that they do this whether caustic potash or caustic soda was actually used to effect the saponification. Whether Dr. Johnstone's protest is sincere, and his grievance serious or paltry, may be judged from the fact that in the very letter in which he formulates his complaint, Dr. Johnstone himself "calculates the glyceryl (C_3H_2) from the amount of KHO consumed," though he actually employed NaHO for the saponification!

In the two experiments on beef fat quoted by Dr. Johnstone, the volume of normal caustic alkali (NaHO) required for saponification was 10·54 and 10·57 c.c., the average of these figures being (according to Dr. Johnstone) 10·56 c.c. But 10·56 c.c. of normal caustic alkali corresponds to $0·0561 \times 10·56 = 0·5924$ grm. of real KHO required for the saponification of 2·5 grms. of beef fat, or 23·696 per cent.

Not having analysed the sample of beef fat in question, I should not presume to pronounce Dr. Johnstone's figures inaccurate. I simply point out that his result (23·7 per cent of alkali, in terms of KHO, required for saponification) is not in accordance with the united experience of other observers that the "alkali-number" for beef fat ranges from 19·3 to about 19·8 per cent; and, as Dr. Johnstone's figures were originally given in an article (*Analyst*, xvi., 26) bristling with anomalies, one is disposed to receive them with considerable reserve. There is no "prejudice" in the question at all. It is simply that the balance of evidence is enormously against Dr. Johnstone, and the probabilities equally great that his figures are erroneous.

That Dr. Johnstone does not claim that his method of operating gives anomalous results is evident from his

statement (*Analyst*, xvi., 27) that "working in this manner an accurate estimation of the amount of alkali required for saponification is obtained, and from which (*sic*) the Koettstorfer number of the fat is readily calculated."

It is difficult to understand Dr. Johnstone's object in quoting his figures, original and recent, for the total percentage of fatty acids obtained from the beef fat ; and the course is objectionable as being liable to obscure the actual point at issue. Dr. Johnstone is perfectly aware that I have not even referred to his determinations of fatty acids, much less ridiculed or described them as anomalous or inaccurate ; nor have I hitherto commented on his annexation of the name "glyceryl" for his imaginary radical C_3H_2. It is a matter which chemists can all appreciate for themselves.—I am, &c.,

ALFRED H. ALLEN.

Sheffield, November 28.

"ALLOTROPIC" SILVER.

To the Editor of the Chemical News.

SIR,—My attention has just been directed to the communication on this subject by Mr. Carey Lea, called forth by some remarks of mine in the Cantor Lectures delivered last spring before the Society of Arts. I should be extremely sorry if Mr. Carey Lea imagines—as would appear from the tone of his communication—that I desired in any way to detract from the value of his most interesting observations. He is labouring under a complete misapprehension if he supposes that I intended to call in question the existence of the coloured compounds or modifications of silver with which he has made us familiar. He is, moreover, inaccurate in stating that my strictures were not based on any "adequate study of the subject," and that "no experimental support of any sort is given." If he will do me the favour of turning to the lectures in question he will find that my statement was : "After carefully considering the conditions of formation, *and after repeating some of the experiments*, I must say that there appears to me to be no sufficient evidence that these coloured forms consist of the pure metal. On the contrary, all the evidence goes to show that some impurity is present, &c." I may add that, following Mr. Carey Lea's instructions, I have not had the slightest difficulty in preparing the gold-coloured product ; with the soluble or colloidal silver I have not been so successful. I freely confess, however, that my experiments have not been numerous in this direction. But since other investigators have succeeded in preparing the "soluble silver" I must attribute my own failure to hurried work or to some violation of Mr. Carey Lea's instructions. I may state also that I am not singular in this failure to produce the "soluble" form, as several other and more experienced operators have met with the same negative results. Mr. Carey Lea would be conferring a boon upon large numbers of chemists in this country who are interested in his work if he would favour us with more explicit instructions.

The facts are that Mr. Carey Lea, by reducing silver salts under certain conditions, has produced certain coloured products which contain a large percentage of silver and a small percentage of other substances. None of the evidence goes beyond this,—not even the most recent contribution to the subject by Schneider, which appears in the number of the *Berichte* just received. One of these products is soluble in water.

Now, I never called in question the existence of these compounds ; I did not even bring forward my own and other experimenter's failures as negative evidence. I only thought it right to caution my audience against applying the term "allotropic silver" to these products. I venture to reiterate that caution now in the hope that Mr. Carey Lea will admit its justice. Allotropy I under-

stand to denote "the appearance of *one and the same substance* (italics mine) in several different states, distinguished from each other by different properties," (Watt's Dictionary, Morley and Muir, vol. i., page 128). How, then, can we apply this term to products which have not yet been shown to be "one and the same substance," viz., silver ?

If Mr. Carey Lea will prepare specimens of his gold-coloured silver or colloidal silver possessing all the properties of these substances, and containing 100 per cent of silver, I will admit the applicability of his term. In the meantime I consider the designation "allotropic silver" to be premature and apt to mislead. In other words I must remain, and I think other chemists will remain with me, in the same position as that which I felt it necessary to take in the Cantor Lectures.—I am, &c.,

RAPHAEL MELDOLA.

Finsbury Technical College,
Nov. 27, 1891.

STUDIES OF SAPONIFICATION.

To the Editor of the Chemical News.

SIR,—In one of his recent letters to you Mr. Allen said that he was attempting to repeat my experiment of heating slaked lime with butter-fat, and, under cover of asking for directions in order to get over an imaginary practical difficulty, contrived to insinuate a contradiction of the initial fact which I had observed and announced.

That initial fact is, that when dry hydrate of lime and dry butter-fat are heated together in an open vessel in the water-bath, chemical action takes place in the absence of any solvent. It is very possible, indeed, that under these conditions a *complete reaction* may not take place, but my experiment showed that a very considerable quantity of the butter-fat had undergone chemical change, and that fact alone is noteworthy and of some importance.

The proof of the occurrence of the chemical action is the loss of weight which I recorded. Inasmuch as butter-fat is not volatile in the water-bath, and hydrate of lime is neither volatile nor decomposable in the water-bath, it is obvious that the escape of any volatile material must indicate the occurrence of chemical change.

Now, to speak quite plainly, I want to know whether Mr. Allen found the loss of weight, or whether he found that there was no loss, or whether he considered that the fact of loss of weight was too trivial to be worthy of his attention.

Instead of an answer to this question, all that I have hitherto been favoured with is the statement that so far as is known, "simply melted butter with slaked lime in suspension" is all that has been observed. Under these circumstances Mr. Allen will understand that his four or five columns of criticism of the opening portion of my paper read to the Society of Chemical Industry in January is looked upon as amusing, but not otherwise as requiring my immediate attention. At present I shall content myself with pointing out that the possibility of action between the carbonic acid of the atmosphere and the materials heated in the open platinum dish was before my mind when I carried out the experiment on saponification by means of dry hydrate of lime, and I ascertained that, like dry hydrate of potassium, dry hydrate of lime is inactive towards carbonic acid. I took much trouble to ascertain the behaviour of the lime, and in one of my experiments found that after a year's exposure to the atmosphere, a specimen of slaked lime was found to contain only 1·4 per cent of carbonic acid.

Towards the end of his paper Mr. Allen makes a statement of a "peculiar and strictly personal" kind. I invite him to refer to the *Chemical Society's Journal*, date 1867, p. 170, where he will find a paper of mine on the "Titration of Compound Ethers," which will probably open his eyes to the fact that some of the "improvements in the analytical

methods of examining fats," which he and his friends imagine to be new, were anticipated by me nearly a quarter of a century ago, and that, being the inventor of the method to which he refers, I am more keenly alive to its limitations than some of those persons who are using it daily in a machine-like manner.—I am, &c.,

J. ALFRED WANKLYN.

Nov. 30, 1891.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxiii., No. 20, November 16, 1891.

Formation of Hydrazin and Azohydric Acid.— MM. Berthelot and Matignon.—A thermo-chemical study. The authors regard hydrazin as a feeble base comparable to ferric oxide, the neutralisation-heat of which is much below that of ammonia and even of hydroxylamine. These three bases represent the three hydrides of nitrogen, but they are not strictly comparable, their condensation being unequal, and one of them constituting a stable hydrate which tends to increase its alkaline character. Azohydric acid, or diazoamine N_3H, is, when diluted, an acid comparable in energy to the amidic acids and superior to hyponitrous acid.

Oxidation of Nickel Carbonyl.—M. Berthelot.—This compound behaves like a true organic radicle. It may be preserved in a bottle under a layer of water without alteration, so long as the air does not penetrate. If air finds access the compound is slowly oxidised, forming at the lower part a layer of nickel oxide of an apple-green.

Action of Light upon Ruthenium Peroxide.—A. Joly.—This compound, RuO_4, improperly called hyperruthenic acid may be preserved indefinitely in a sealed tube if perfectly dry. The least trace of water decomposes it, forming an intermediate oxide, Ru_2O_5, with escape of oxygen. The sides of the tube, if not kept in total darkness, assume a metallic lustre, which is proved by experiment to be due to light alone. The product of the reduction of the peroxide is the teroxide, RuO_3.

Certain Saline Compounds of the Lower Oxygen-Compounds of Ruthenium with Ruthenic and Heptaruthenic Acids.—A. Joly.—Potassium ruthenate is a new " mineral chameleon." If the heptaruthenate is heated to 440° in a vacuum, it is abruptly decomposed, liberating oxygen, being converted either into a mixture of ruthenate and ruthenium dioxide, or into a compound of potassium with a lower oxide. If these decomposition products are kept at 440° for a sufficient time they react upon each other, yielding a black, crystalline compound, quite distinct from the dioxide. Its composition is that of an acid salt, $KO,6Ru_2O_5$. Water removes from the mixture potassa and potassium ruthenate. Sodium heptaruthenate, NaO,Ru_2O_7+2HO, if heated to 440°, suddenly loses oxygen and water, and if treated with water and orange rutheniate and soda are dissolved, and there remains a black, crystalline powder, the composition of which is close upon $NaO,3Ru_2O_5$. Barium ruthenate, BaO,RuO_3, behaves differently at 440°. Oxygen is lost, and the residue, BaO,RuO_2, is a ruthenite, which, from its reactions, cannot possibly be considered as a mere mixture of baryta and of the dioxide.

Iodonitric and Bromonitric Platinum Salts.—M. Vèzes.—The author has previously described several platinum chloronitrates and bromonitrates, between the platinonitrite $Pt_4NO_2K_2$ and the saturated haloid salt $PtX_4.K_2X_2(X=Cl,Br)$. In hot solutions of iodonitrates

the iodine in these bodies is displaced by nitrous products, so that the most stable term of the iodine series is the platinonitrite and not the iodoplatinate. The author has obtained potassium nitrosoiodoplatinate, $Pt.I_3.NO.K_2I_2$; potassium platitetraiodonitrite, $Pt.I_4,2NO_2.K_2$, and potassium bromonitrite, $Pt.2NO_2.K_2.Br_2+H_2O$.

The Colouration of the Solutions of Cobalt, and the State of the Salts in these Solutions.—A. Etard. —The author expresses his conclusions by means of the graphic method.

Nitrised Milk.—Leo. Vignon and P. Sisley.—The authors find that the yellow colouration which nitric acid occasions in silk is best obtained by dipping and rapidly smoothing out the silk for about a minute in a mixture of water and nitric acid, specific gravity 1·133 at 45°. After washing in a large excess of water the silk preserves a very characteristic yellow colour, fast to air and light ; the colour is much darkened on immersion in alkaline liquids, but may be restored to its original shade by treatment with acids. Pure nitric acid under the above conditions does not colour silk. If a little sodium nitrite is added to pure nitric acid the yellow colour is produced. The reaction, which gives a fast yellow colour on silk, requires the presence of NO, NO_2, or NO_2H, and contact with nitric acid as an oxidiser.

Moniteur Scientifique, Quesneville.
Series 4, Vol. iv., Part 2, No. 588.

Synthesis of Citric Acid.—A. Haller and A. Held.— Syntheses of this acid have been previously effected by Grimaux and Adam, then by Prof. Kekulé, and lastly by Herr Dunschmann. The present authors demonstrate the conditions under which may be effected the synthesis of acetondicarbonic ether, and subsequently that of citric acid. The synthetic citric acid presents all the physical, organoleptic, and chemical characters of the natural acid. The crystals melt at 100°.

Azohydric Acid, N_3H, or Azoimide.—Herr Th. Curtius.—The author has obtained this compound, which in all its reactions behaves like a hydracid of the haloid family. It is a gas of a peculiar and very pungent odour. It is energetically absorbed by water, and even in dilute solutions it irritates the mucous membranes and occasions headache. It reddens litmus paper, and forms with gaseous ammonia dense white fumes. In a 7 per cent solution it dissolves iron, zinc, copper, aluminium, and magnesium, with a tumultuous liberation of hydrogen. More concentrated solutions seem even to attack gold and silver, for the liquid becomes red. Silver and mercurous nitrates give with dilute azohydric acid precipitates of silver and mercurous azoimide. Azohydric acid does not precipitate the other metallic salts.

Researches on the Devitrifying and Dissolving Action of Water upon Acids.—(No author's name).— The easy devitrification of a glass is not simply due to an excess of lime, but is a function of the ratio existing between simple sodium silicate and acid calcium silicate. This proportion is 0·40 in stable glass, and 0·28 in glasses which are easily devitrified. Glasses with multiple bases are the less easily vitrified the greater the number of bases entering into their composition. It will be easy for the glass-makers to obtain calcareous clays of such a composition that for bottles it will be merely necessary to add sand and a little alkali. For optical glass alumina and iron must be absolutely rejected, and the only available materials are silica, lime, and alkali. From 100 grms. of glass used for glow-lamps water dissolved 3·974 grms. of alkali, besides traces of alumina, ferric oxide, and lime.

On Tanning Woods.—J. J. Arnaudon.—Carolina sumac, the leaves of *Rhus glabra*, is used in tanning, but its proportion of tannin is not stated. Copaline sumac

(*Rhus copalinum*) contains rather less tannin than *Rhus glabra*. Both the above species of sumac are of American origin. Chinese sumac (*Rhus semialata*) is the bark of a tree upon which the Chinese gall-nuts are produced. Fustet or scotano is the wood of *Rhus cotinus* (known in England as young fustic). The best quality comes from Greece and the Ionian Islands. Sumac of Tezera, or of Africa (*Rhus pentaphylla*): a grey bark used in the north of Africa for dyeing and tanning. Egyptian sumac (*Rhus oniyacantha*) grows in Egypt and Asia Minor. The bark of the root is employed in tanning. *Rhus lucida*, shining-leaved sumac, *Rhus thunbergi*, *Rhus levigata* and *viminalis* are produced at the Cape. *Rhus rhodanthema* (Queensland sumac) and *Rhus elegans* (also from Australia) are used in dyeing and tanning.

Experimental Researches on the Electrolytic Preparation of Sodium and Aluminium.—A. J. Rogers.—(From the CHEMICAL NEWS).

Metallurgical Use of Aluminium and Ferroaluminium (*Dingler's Polyt. Journal*).—G. Arth.—An account of the use of aluminium in increasing the fluidity of melted iron and preventing blow-holes. Its addition to the melted iron in the converter cannot be recommended on account of the increased expense. A 10-ton Bessemer charge with an addition of 0·1 per cent aluminium will come to 956 francs.

Working Aluminium.—From the *Scientific American*.

The Properties of Aluminium.—A. E. Hunt, J. W. Langley, and C. M. Hall.—From the *Journal of Chemical Industry*.

Tempering and Hardening Steel for Cannon and Projectiles.—Prof. Watson Smith.—From the *Journ. Soc. Chem. Industry*.

On Double Explosions in Puddling Furnaces.—Haedicke (*Stahl and Eisen*).—The author considers that the first of these twin explosions is due to the sudden evaporation of a large quantity of water in consequence of the cessation of the spheroidal state. This first explosion is followed by a partial vacuum in the interior of the apparatus, when there ensues a simultaneous aspiration of air, and of the combustible gases of the furnace,—carbon monoxide and hydrocarbons. This detonating mixture is ignited in contact with the hot walls of the furnace and causes the second explosion.

Practical Researches on Zincing.—B. Preu (*Chem. Zeitung*).—Of three known methods the author prefers one in which the bath is composed simply of zinc, covered entirely or in part with a layer which prevents oxidation. Sal-ammoniac gives the best results, but it evaporates rapidly and has to be renewed frequently. It diminishes the dangers of explosion, but it occasions unpleasant vapours.

Glass and Ceramic Art.—Under this head come accounts of Japanese enamels (*Chemiker Zeitung*), photographic process for decorations in relief (*Sprechsaal*), manufacture of marbled glass (*Sprechsaal*), yellow lining glass, by Hananeck (*Sprechsaal*), new red glass (*Scientific American*), enamels free from lead (*Chemiker Zeitung*).

On Horse-Fat.—L. Lenz (*Chemiker Zeitung*).—Fresh horse-fat, if melted in the water-bath, is yellow and neutral; it has the consistence of butter, and after a few days it becomes viscid. Its weight remains constant for four weeks, then it gained 0·691 grm. in the first year and 0·201 in the second, after which its weight remained constant. The original weight of the sample was 22·521 grms.

Oxidation of Gallic Acid, of Tannin, and of the Tannic Acids of the Oak.—Dr. C. Böttinger.—The author on studying the action of nitric acid upon tannin and gallic acid, obtained along with oxalic acid a smaller quantity of two other acids, which may be separated by means of their calcium salts.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. vi., Nos. 4 and 5, September 5, 1891.

On Azothydric Acid.—E. Noelting and E. Grandmougin.—According to the researches of Curtius, diazobenzolimide may be considered as the phenylic ether of azohydric acid. This derivative may easily be prepared by diazotising dinitraniline, transforming it into perbromide, and treating the latter with ammonia. Under the influence of alcoholic potassa it is split up very sharply, yielding potassium salts of dinitrophenol and azothydric acid. On acidifying and distilling there passes over an aqueous solution of azothydric acid, which is identified by means of the characteristic reactions described by Curtius. The authors intend to study the other nitrised diazobenzolimides, and to ascertain the most favourable conditions for the preparation of azothydric acid.

Boron Selenide.—Paul Sabatier.—The author obtains boron selenide by passing a current of very dry hydrogen selenide over amorphous boron, kept at a red heat in a tube of Bohemian glass. The boron is entirely transformed into a yellowish grey selenide, showing no trace of fusion. Beyond the "boat" the sides of the tube are lined with a thin powdery layer of pale yellow boron selenide; further on there are found small drops of vitreous selenium, then of scarlet selenium mixed with a little selenide. The sublimate of yellow selenide is briskly destroyed by water, yielding boric acid and hydrogen selenide. The composition of the selenide is B_2Se_3. A sub-selenide has also been obtained, Bo_4Se. Boric selenide is much less volatile than boron sulphide and even than selenium.

Silicon Selenide.—Paul Sabatier.—This compound was obtained by heating crystalline silicon to redness in a current of dry hydrogen selenide. The conversion takes place without incandescence. The selenide takes the form of a melted, hard, incandescent body of a metallic appearance, which does not appear volatile at the temperature of the experiment. Its composition is $SiSe_2$. Water acts upon it briskly, yielding silica and hydrogen selenide.

Action of Ammonia upon Mercury Cyanide and its Compounds with Haloid Salts.—Raoul Varet.—This paper has been already noticed.

Researches on Lead Chromate.—MM. Lachaud and Lepierre.—Also previously noticed.

Researches on Thallium.—M. Lachaud and C. Lepierre.—The authors describe a series of experiments on thallium chromate prepared by precipitating pure thallous sulphate with neutral potassium chromate. The salt obtained, Tl_2CrO_4, is amorphous and of a lemon-yellow colour. It was treated successively with dilute potassa, concentrated potassa, potassa in a state of fusion, and potassium nitrate. They have also obtained thallium chlorochromate, but not in a state of perfect purity. Reference is made to a new method of determining thallium which is to furnish the subject of future communication.

Determination of Chrome Yellows.—The method proposed by the authors will be given in full.

Molecular Lowering of Phenol.—MM. Juillard and Curchod.—The authors find that the molecular lowering of synthetic phenol, fusible at 41·2°, varies with the nature of the substance dissolved. The mean value is 68·5 for water, β-naphthol, paratoluidine, aniline, nitrobenzene, phthalic anhydride, diphenic anhydride, α-naphthylamine, amylic alcohol, vicinic acid, and anhydrobenzhydrolcarbonic acid. For the neutral ethers, especially the ethers of the bibasic acids, the mean is 75·81. The value 68·5 is the most general experimental lowering, and must consequently be adapted for cryoscopic experiments made with phenol.

Boron Sulphides.—Paul Sabatier.—The action of hydrogen sulphide upon boron heated to redness yields not merely normal boron sulphide, B_2S_3, but also a borous sulphide, B_4S, and a small proportion of a hydrosulphate which is doubtless $B(SH)_3$.

On Picene.—R. Lespieau.—The author finds that the carbide described by M. Roux as—

$$C_{10}H_6 {<}^{C_{10}H_7}_{C_{10}H_7}$$
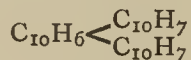
is the picene described by Burg.

Variations of the Colour of Cobalt Chloride.—M. Engel.—This extensive memoir does not admit of useful abstraction.

Researches on the Sulphonic Derivatives formed by the Action of Sulphuric Acid upon Castor Oil.—M. Scheurer-Kestner.—Alizarin oil (oil for reds) is a complex compound, including polymerised fatty acids and sulphones, partly normal and partly desulphonised by the action of the washing waters. The sulphonic acids are present in the state of hydrates. A yellowish " raising " (*arivage*) is occasioned by the sulphonic acids, and a bluish one by acids which are desulphonised but polymerised.

Methæmoglobine derived from Oxycarbonic Hæmoglobine.—H. Bertin-Sans and J. Moitessier.—From the experiments of the authors it may be concluded that the solutions of methæmoglobine obtained by means of oxycarbonic hæmoglobine, or by treating oxygenated hæmoglobine with a current of carbon monoxide, contains simply methæmoglobine and carbon monoxide in solution. If by the action of ammonium sulphide these solutions give oxycarbonic hæmoglobine, it is because the methæmoglobine is transformed into hæmoglobine, which is combined with dissolved carbon monoxide. The authors will shortly publish a process for detecting small quantities of carbon monoxide in blood.

Certain Coloured Reactions of the Carbohydrates.—G. Bertrand.—If we heat gently a glucose with concentrated hydrochloric acid holding in solution a small quantity of phloroglucine (one or two drops of a saturated aqueous solution of this substance to some c.c. of acid), there appears a yellow colour which rapidly passes to an orange-red. On continuing to heat there is formed a dirty red precipitate, and the liquor is partly decolourised. This reaction is produced also in the cold, but it then requires several hours. The author finds that the red colouration mentioned above is obtained with all the glucoses and with bodies capable of forming such on hydration. But the hydrochloric acid must be strong, about 1·18. With orcine and hydrochloric acid an orange-red liquid is yielded by Soxhlet's glucose, the glucose of cellulose, galactose, mannose, levulose, sorbine, saccharose, lactose, maltose, raffinose, melizitose, stachyose, trehalose, isodulcite, glycogene, inuline, levuline, potato-starch, rice-starch, dextrine (commercial), achroodextrine, amygdaline, salicine, hesperidine. The following give a violet-blue liquid:—Arabinose, xylose, cherry-gum, strowgum, gum of pines, gums arabic and senegal (the two latter a violet red). The following yield no colouration :—Xylite, sorbite, dulcite, mannite, perseite, inosite, penite, bergenite, Peligot's saccharine.

The Acidity of Green Grapes and the Preparation of Malic Acid.—Ch. Ordonneau.—Unripe grapes and grapes from certain climates (*e.g.*, Vendée) contain much malic acid. Wine from Vendée yielded in 1890 more than 15 grms. of tartro-malate per litre. In certain white wines malic acid is present in greater quantity than the total tartaric acid. The author proposes to obtain malic acid from the dregs remaining on distilling wines.

The Hydrates of Cobalt Chloride and the Changes of Colour of this Compound.—A. Potilitzine.—The author considers that the changes of colour depend on the dissociation of a hydrated salt, or on the elimination of water.

THE CHEMICAL NEWS.

VOL. LXIV., No. 1672.

A CALCIUM PHOSPHATE DEPOSITED FROM AN ACETIC ACID SOLUTION.

By HERBERT E. DAVIES, B.A., B.Sc.

IF the precipitate obtained by adding ammonia to a hydrochloric acid solution of tri-calcium phosphate be dissolved in acetic acid, and the solution kept for some days, crystals begin to deposit and continue to do so for some time.

Having obtained about 2 grms. of these crystals, I washed them thoroughly with water and then dried them in vacuo over sulphuric acid for about four days. They then appeared as brightly glittering prismatic crystals.

On heating them in the water-oven for several hours they only lost weight to a very slight extent (0·85 per cent), and prolonged heating to a bright redness in the muffle was necessary before they ceased to lose weight.

Analysis of the crystals as dried over sulphuric acid gave the following result :—

Ca	..	..	..	22·86
P	..	..	..	18·08
O	..	..	..	56·06
H	..	..	..	2·94
				99·94

From this the formula CaH_5PO_6 is calculated. A substance having the same percentage composition is described by Groves as being formed when Na_2HPO_4 is added, drop by drop, to an excess of $CaCl_2$, but its properties, as described by him, differ from those of the compound prepared as above.

From the fact that there is practically no loss of water when heated to 100° C., and, further, that there is no definite temperature at which two molecules of water are lost, together with the fact that a large proportion of the loss occurs only at a very high temperature, it seems probable that the compound does not contain water of crystallisation. If this be so it seems as though the compound were a derivative of the maximum hydroxide of phosphorus $P(OH)_5$. If we suppose this to react with the hydroxide of calcium, $Ca(OH)_2$, and one molecule of water to be lost we get—

$$
\begin{array}{c}
P(OH)_4 \\
| \\
O(CaOH)
\end{array}
$$
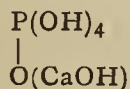
as the formula of the body.

The Royal Institution Laboratory,
Liverpool.

ON CHEMISM IN LIVING PROTOPLASM.

By Prof. W. PREYER and G. WENDT (of Berlin).

(Continued from p. 275).

THE assimilation and dissimilation of matter, both constantly manifested in living protoplasm can be nothing other than chemical processes, since true transmutations of matter, *i.e.*, chemical combinations externally and internally different, can be produced only by atomistic reactions. Otherwise the very foundations of chemical science would be insecure.

The first five of the six essentials—attendant phenomena of every chemical reaction—have been directly observed or experimentally demonstrated as the fundamental functions of protoplasm ; but not the sixth—the chemical action of mass.

On the basis of his experiments on the dead space in chemical reactions, Liebreich concludes that " the occurrence of every chemical reaction is possible only in excess of a certain definite magnitude of the space in which it is to ensue." It cannot be denied that in capillary spaces the physical influence of the enclosing sides and the various tension of the liquid surfaces are magnitudes which must be carefully taken into account. Almost all capillary reactions, as it is well known, are exceedingly sensitive. It has long ago been decided that these values, which may be neglected under ordinary circumstances, are very considerably modified on quite minute alterations of spacial relations, of the surface of the sides, the physical properties of the liquids concerned, and on the slightest impurities or admixtures ; as also on very trifling modifications of temperature, or illumination, &c. Hence it is intelligible that in such variations, which seem quite insignificant for the conditions of the laboratory, important alterations must ensue in capillary reactions. Hence the exact repetition of such experiments becomes an exceedingly difficult problem. Even an exact statement of the conditions of an experiment is often almost impossible.

In consequence of this conclusion an ordinary chemical reaction can scarcely be imagined in a microscopic test-tube, in a microscopic retort, or in a microscopic flask. Liebreich says very briefly that " a certain size " of the cell spaces is needed if a quite different, and in a manner degenerate, chemical process is not to ensue.

What is to some extent a degenerate chemical process is not intelligible, but in any case our assumption, which agrees perfectly with the first words, appears admissible, namely, that in microscopical protoplasm there are always spaces where a chemical action of mass does not reach validity in opposition to very strong physical influences, though nevertheless intense chemical reactions take place. But where there is no chemical action of mass in protoplasm, the effort towards chemical equilibrium cannot be present. The important formula of Guldberg and Waage—$k_1 p_1 q_1 = k_2 p_2 q_i$, the law of the chemical action of mass—which is not only inductively derived by experiment, but also deductively from the mechanical theory of heat, does not then hold good for the specific chemism of protoplasm.

This law may be most briefly expressed as follows :—

If p_1 and p_2 signify the relative quantities of the free bases, and q_1 and q_2 the quantities of the two salts formed in molecular weights, and k_1 and k_2 constants depending on the mutual affinities of the bases and the salts to each other, the energy with which the two antagonistic reactions tend to be effected may be expressed by $k_1 p_i q_2$ and $k_2 p_2 q_i$. The main law of the chemical action of mass is then expressed by the formula $k_1 q_i_1 q_2 = k_2 p_2 q_1$,—that is, each of the two antagonistic reactions tend to be carried out with an intensity proportional to the relative quantity of the matters concerned or to the number of their mols., and equilibrium is reached at that proportion of quantities at which the opposing forces become equally great.

That this law cannot hold good for living protoplasm follows from the microscopic smallness of the protoplasmic tissues, which display the most intense metabolism, and the unparalleled variability of protoplasmic matter.

However different are the opinions of the best observers as regards the nature of protoplasm, all, doubtless, agree that protoplasm, whether it is found in the Amœba living freely in the water, or in the Leucocytes circulating in the plasma of the blood in the sluggish corpuscles of conjunctive tissue, or in the briskly moving cholera bacillus, or in the nucleus of an ovum, in a ganglionic globule, or in a glandular cell, is extremely complicated, and not, as was formerly supposed, homogeneous ; not a mucoid, an albumenoid, nor indeed a matter of whatever kind, but that it is exactly characterised by its changes of material, of forces, and of form.

Protoplasm is no chemical compound (to aim at proving this would, in our day, be mere trifling) ; it is also no simple mixture of chemical compounds as long as it breathes, assimilates, moves, and developes ; for we do not call a working machine a simple mixture of the combinations or elements of which it is constructed, or which it takes in and gives out.   It is also no mixture of chemical compounds, for we easily recognise for the most part in protoplasm heterogeneous parts, independent of the nucleus of the vacuolæ, and of differentiated appended structures.   It is altogether no structure which, on mechanical or ultimate analysis, yields constant relative quantities of the substances which pre-exist in it, or which may be obtained from it, carbon, nitrogen, hydrogen, phosphorus, sulphur, calcium, &c., but it has an inconstant composition.

(To be continued).

THE BEHAVIOUR OF AZOIMIDE WITH LIVING ORGANISMS.*

By O. LOEW.

(Continued from p. 276.)

When 1 grm. of scraped meat was placed in a flask and covered with 20 c.c. of a 1 per cent solution of sodium azoimide, it remained unchanged, and did not putrefy even if infected with schizomycetes.   In a check flask, offensive putrefaction set in after twenty-four hours, effected by a multitude of bacteria in brisk movement.

4. *Experiments with Hyphomycetes.*

To 50 c.c. of a cultivation liquid of the same composition as that used in the experiments with bacteria, there was added, beside 1 part per 1000 sodium azoimide, 2 parts per 1000 mono-potassium phosphate, and the liquid was then infected with the spores of *Penicillium* and *Aspergillus*.   But even after some weeks not a trace of the mycelium of mould was developed, even if di-ammonium phosphate was present in addition to sodium azoimide.

Another nutrient solution, which instead of a tartrate contained 5 parts per 1000 of glucose, and also 0·5 per 1000 of sodium azoamide, developed even after many weeks not a trace of the filaments of mould, in spite of infection and exposure to the air.   A check specimen, which contained nitrogen in the form of 0·5 per 1000 ammonium chloride, developed on the third day a thin film of mould along with a bacterial turbidity, and on the eighth day a considerable layer of mould.

5. *Experiment with Saccharomycetes.*

A portion of pressed yeast of the size of a pea was shaken up with 10 c.c. of water ; one half of the liquid was mixed with 5 parts per 1000 of sodium azoimide, and the other was let stand for two days without this addition.   The latter portion had already an offensive smell, and the supernatant liquid contained numerous bacilli ; the former was inodorous and free from bacilli.   The yeast which had settled to the bottom was brought in contact in a narrow tube with about 5 c.c. solution of glucose.   In both cases fermentation was set up in about 25—30 minutes, though less briskly in the portion which had been treated with sodium azoimide.

Saccharomycetes are, therefore, more resistent than schizomycetes and hypomycetes, as has been already shown in many other cases.   Whether the poison here penetrates less readily or whether protective arrangements exist in the protoplasm remains for the present undecided.

6. *Experiments with Infusoria.*

If a drop of a 1 per cent solution of sodium azoimide

* *Ber. Deutsch. Chem. Gesell.*

is brought in contact with infusoria under the microscope, there is a sudden cessation of all vital movements.   A 0·1 per cent solution in spring water does not cause the movements to cease in less than 2—2½ hours.   In the Vorticellæ there sets in firstly partial paralysis, when the stem and the cilia become rigid.   In Stylomychia the movements become for a short time very violent before they cease altogether.   Other Infusoria contract to motion-less globules, whilst the Euglenæ twist backwards and forwards for some time before life ceases.   If, accidentally, species of Cyclops (belonging to the Crustacea) are found among the infusoria, their rapid movements are quickly paralysed until life is entirely extinguished.

If the solution is diluted with 10 parts of water, living Vorticellæ and Amœbæ may be observed even after twelve days.

7. *Experiments on Various Aquatic Animals.*

In a 0·5 per mille solution of sodium azoimide in well water, Nematodes, Planariæ, Ostracodæ, Copepods, wood lice, small insect larvæ, and young snails (*Planorbis, Limnæa*) die in 30—40 minutes.   In 2½—3 hours small water-beetles die ; leeches later.

In a 0·1 per 1000 solution Crustaceans die in 20—24 hours, death being preceded by paralysis.   Water-beetles and snails die after four days ; leeches and insect larvæ were still living after six days.

8. *Experiments on Mammalia.*

Prof. Emmerich, of the Hygienic Institute, here kindly made a few experiments, and reports as follows :—

"Your conjecture concerning the action of sodium azoimide is fully confirmed.   The subcutaneous injection of 1 c.c. of the 1 per cent solution caused in a large mouse in ten seconds sudden cramps, emprosthotonus, and instant death.   Even 0·1 c.c. injected into a mouse subcutaneously occasioned in three minutes cramp of the diaphragm, and within four minutes paralysis of the extremities.   In two minutes more there set in clonic cramps of all the muscles, emprosthotonus, and death.   On the immediate opening of the thorax, the auricles contracted a few times, and the heart then became still.   The blood was very dark."

(To be continued).

DETERMINATION OF SMALL QUANTITIES OF ALKALI AND RECOGNITION OF THE NEUTRALITY OF WATER.

By F. MYLIUS and F. FOERSTER.

(Concluded from p. 277).

The figures signify thousandths of a m.grm., and show that the factor ascertained for soda is sufficiently accurate for potassa and ammonia.   From all this it follows that our colorimetric method suffices to determine even 0·005 alkali with some accuracy.

For the appreciation of the colorimetric method as well as for that of titration with mille-normal solutions, we require a knowledge of the influence of carbonic acid upon the determination of very small quantities of alkali, the more so as our experiments for the determination of the empirical fact r above mentioned were made with a solution of sodium carbonate instead of with one of pure sodium hydroxide.   "Neutral" water was therefore saturated with carbonic acid obtained by heating sodium bicarbonate.   A saturated solution of carbonic acid contains about 0·9 grm. carbonic acid per litre.   This solution was mixed in various proportions with neutral water, and known quantities of soda were added to the mixture.   The red colour obtained in the solutions of alkali thus obtained, after shaking out with ethereal solution of eosine and with aqueous ether, was determined.   The results were as

follows:—In presence of 0·05 m.grm. Na_2O in 100 c.c. water, which had required 55 c.c. of the alkaline solution of eosine, there were found on the simultaneous presence of—

9·7 equivs. CO_2	..	..	52·3 c.c. solution of eosine.
16·0 ,,	..	..	49·0 ,, ,,
27·0 ,,	..	..	42·8 ,, ,,
128·0 ,,	..	..	27·3 ,, ,,

We see that, as it might have been expected, the influence of carbonic acid when in large excess is very considerable, whilst a moderate excess is of little importance. We shall not be deceived if we assume that the small possible fluctuations of the quantity of carbonic acid always present in water, as they are produced by the use of solutions of sodium carbonate instead of soda-lye, have scarcely any influence upon our colorimetric determinations of alkali. This result was to be anticipated in view of the large excess of eosine always present in the determinations, and of the above mentioned indifference of carbonic acid on titration with dilute solutions, using very small quantities of iodeosine. The fact that the figures referring to ammonia in the above conspectus show the same agreement as those referring to potassium and sodium carbonate agrees with what has been above mentioned.

A few instances may be given to show the applicability of the colorimetric method. With its aid the determination of ammonia can be effected with some degree of accuracy even in dilutions in which Nessler's reagent scarcely admits of a qualitative conclusion as to the presence of ammonia. When distilled water from Kahlbaum (a dealer in pure reagents) was distilled with soda, each 100 c.c. of three successive portions of the distillate represented 10 c.c. of the eosine solution, which would correspond to 0·0274 m.grm. ammonia per litre of the distillate.

The colorimetric method for the determination of alkali permits by reason of its great sensitiveness a determination of the quantities of alkali extracted by aqueous liquids from glass vessels in which they have been kept. We mention a series of experiments in order to show the changes which water undergoes when kept in a glass bottle. The bottle held about 1 litre, and consisted of good glass; it had been well rinsed out with water before the experiments. When neutral water was kept in it for some time, successive portions of the water of 100 c.c. each showed the following values:—

1 day, 15 c.c. solution of eosine	= 0·0094 Na_2O.
3 ,, 21·5 ,, ,,	= 0·017 ,,
8 ,, 32·3 ,, ,,	= 0·027 ,,

The method of determining alkali which we have here proposed may be used for the determination of the alkaline earths in the same manner as for the alkalies. As it is easily seen, small quantities of mineral acids may be also determined colorimetrically if we make use of alkaline solutions of known strength according to the practice of volumetric analysis. A somewhat wide field is therefore open for the applicability of the method. It may also be occasionally useful in the examination of animal and vegetable liquids as also in the investigation of minerals. In this direction an experiment may be mentioned which was executed to observe the decomposability of potassic felspar by water. 5 grms. of coarsely powdered orthoclase prepared by picking, sifting, and repeatedly washing away the adhering dust, were left for forty-eight hours in contact with 100 c.c. of neutral water at a common temperature in a platinum flask. At the end of this time 0·018 m.grm. potassa (K_2O) had passed into solution, as it was concluded from the intensity of the colour on examination.—*Berichte der Deutsch. Chem. Gesell.*, vol. xxiv., p 1482.

NINTH ANNUAL REPORT OF THE COMMITTEE ON INDEXING CHEMICAL LITERATURE.*

THE Committee on Indexing Chemical Literature respectfully presents to the Chemical Section its ninth annual report.

Since our last meeting the following bibliographies have been printed:—

1. "A Bibliography of Geometrical Isomerism." Accompanying an address on this subject to the Chemical Section of the American Association for the Advancement of Science at Indianapolis, August, 1890, by Prof. Robert B. Warder, Vice-President. *Proc. A. A. A. S.*, vol. xxxix., Salem, 1890. 8vo.

2. "A Bibliography of the Chemical Influence of Light," by Alfred Tuckermann. Smithsonian Miscellaneous Collections, No. 785, Washington, D.C., 1891. pp. 22, 8vo.

3. "A Bibliography of Analytical Chemistry for the Year 1890," by H. Carrington Bolton. *Jour. Anal. Appl. Chem.*, v., No. 3. March, 1891.

We chronicle the publication of the following important bibliography.

"A Guide to the Literature of Sugar." A book of reference for chemists, botanists, librarians, manufacturers, and planters, with comprehensive subject-index. By H. Ling Roth. London: Kegan Paul, Trench, Trübner, and Co., 1890. 8vo., pp. xvi.—159.

This work contains more than 1200 titles of books, pamphlets, and papers relating to sugar. Many of the titles are supplemented with brief abstracts. The alphabetical author-catalogue is followed by a chronological table and an analytical subject-index. The compilation extends to the beginning of the year 1885, and the author promises a supplement and possibly an annual guide.

This ambitious work is useful but very incomplete; it does not include glucose. The author gives a list of fifteen periodicals devoted to sugar, and omits exactly fifteen more recorded in Bolton's *Catalogue of Scientific and Technical Periodicals* (1665—1882). (Washington, 1885.) Angelo Sala's *Saccharologia* (Rostock, 1637), is not named, though mentioned in Roscoe and Schorlemmer and elsewhere. Notwithstanding some blemishes, this work is indispensable to chemists desirous of becoming familiar with the literature of sugar. It is to be hoped that a second edition brought down to date may be issued by the author.

4. "A Bibliography of Ptomaines" accompanies Prof. Victor C. Vaughan's work. "Ptomaines and Leucomaines," Philadelphia, 1888. (Pages 296—314). 8vo.

Chemists will hail with pleasure the announcement that a new "Dictionary of Solubilities" is in progress by a competent hand. Prof. Arthur M. Comey, of Tuft's College, College Hill, Mass., writes that the work he has undertaken will be as complete as possible. "The very old matter, which forms so large a part of Storer's Dictionary, will be referred to, and in important cases fully given. Abbreviations will be freely used, and formulæ will be given, instead of the chemical names of substances, in the body of the book. This is found to be absolutely necessary, in order to bring the work into a convenient size for use. . . . The arrangement will be strictly alphabetical. References to original papers will be given in all cases . . ."

Professor Comey estimates his work will contain over 70,000 entries, and will make a volume of 1500 to 1700 pages.

The following letter from Mr. Howard L. Prince, Librarian of the U.S. Patent Office, explains itself.

UNITED STATES PATENT OFFICE,
Washington, D.C., February 11, 1891.

DR. H. CARRINGTON BOLTON, University Club, N.Y.

DEAR SIR,—In response to your request I take pleasure in giving you the following information regarding the past accomplishments and plans for the future of the Scientific Library in the matter of technological indexing.

The work of indexing periodicals has been carried on in the Library for some years in a somewhat desultory fashion, taking up one journal after another, the object being, apparently, more to supply clerks with work than the pursuance of any well-defined plan. However, one important work has been substantially completed, viz., a general index to the whole set of the *Scientific American* and Supplement from 1846 to date.

It is unnecessary for me to point out to you the importance of this work, embracing a collection which has held the leading place in the line of general information on invention and progress, the labour of compiling which has been so formidable that no movement in that direction has been attempted by the publishers, except in regard to the supplement only, and that very imperfectly. This index embraces now 184,000 cards, not punched, and at present stored in shallow drawers and fastened by rubber bands, and, of course, they are at present unavailable for use. There is little prospect of printing this index, and I have been endeavouring for some time to throw the index open to the public by punching the cards and fastening them with guard rods, but as yet have made no perceptible impression upon the authorities, although the expense of preparation would be only about 70.00 dollars.

There has also been completed an index to the English journal *Engineering*, comprising 84,000 cards, from the beginning to date.

An index to *Dingler's Polyt. Jour.* was also commenced as long ago as 1878, carried on for six or seven years and then dropped. I hope, however, at no remote date, to bring this forward to the present time.

On taking charge of the library I was at once impressed with the immense value of the periodical literature on our shelves, and the great importance of making it more readily accessible, and have had in contemplation for some time the beginning of a card index to all our periodicals on the same general plan as that of Rieth's Repertorium. I have, however, been unable to obtain sufficient force to cover the whole ground, but have selected about 150 journals, notably those upon the subjects of chemistry, electricity, and engineering, both in English and foreign languages, the indexing of which has been in progress since the 1st of January. This number includes substantially all the valuable material in our possession in the English language, not only journals, but transactions of societies, all the electrical journals, and nearly all the chemical in foreign languages. This index will be kept open to the public as soon as sufficient material has accumulated. In general plan it will be alphabetical, following very nearly the arrangement of the periodical portion of the Surgeon-General's catalogue. I shall depart from the strictly alphabetical plan sufficiently to group under such important subjects as chemistry, electricity, engineering, railroads, &c., all the subdivisions of the art, so that the electrical investigator, for instance, will not be obliged to travel from one end of the alphabet to the other to find the divisions of generators, conductors, dynamos, telephones, telegraphs, &c., and in the grouping of the classes of applied science the office classification of inventions will, as a rule, be adhered to, the subdivisions being, of course, arranged in alphabetical order under their general head, and the title of the several articles also arranged alphabetically by authors or principal words.

With many thanks for the kind interest and valuable information afforded me, I remain,

　　　　　　　　Very truly yours,
　　　　　　　　　　HOWARD L. PRINCE,
　　　　　　　　　　Librarian Scientific Library.

The committee much prefers to record completed work than to mention projects, as the latter sometimes fail. It is satisfactory, however, to announce that the indefatigable indexer, Dr. Alfred Tuckerman, is engaged on an extensive " Bibliography of Mineral Waters." The Chairman of the Committee expects to complete the MS. of a " Select Bibliography of Chemistry " during the year, visiting the chief libraries of Europe for the purpose this summer.

　　　　　　H. CARRINGTON BOLTON, *Chairman.*
　　　　　　F. W. CLARKE.
　　　　　　ALBERT R. LEEDS.
　　　　　　ALEXIS A. JULIEN.
　　　　　　JOHN W. LANGLEY.
　　　　　　ALBERT B. PRESCOTT.

(Dr. Alfred Tuckerman was added to the committee at the Washington Meeting to fill the vacancy).

ON THE OCCURRENCE OF NITROGEN IN URANINITE, AND ON THE COMPOSITION OF URANINITE IN GENERAL.*

By W. F. HILLEBRAND.

(Continued from p. 281).

IN the following table all the foregoing analyses o Norwegian material have been re-calculated to the percentages found, excluding the insoluble matter, in order that their true relations may appear at a glance, whereby the sum of the rare earths combined is given instead of each earth or group of earths by itself. Only those constituents are tabulated which may be considered unquestionably in whole or in part as belonging to the uranium mineral. Silica, ferric or ferrous oxide as it may be, the small amounts of magnesia, alkalies, &c., may be thrown out as derived from admixed impurities. Lime from its close relationship to the other earths has been retained, though it is undoubtedly, in part at least, derived from foreign silicates.

TABLE V.—*Analyses of Norwegian Uraninite Re-calculated.*

	XII.	XIII.	XIV.	XV.	XVI.	XVII.	XVIII.
UO_3..	32·04	25·48	26·04	32·50	35·69	42·11	27·12
UO_2..	48·25	50·97	50·83	44·57	43·56	24·51	44·71
Earths	7·97	10·18	9·96	10·64	8·12	13·57	14·03
PbO..	9·45	10·11	10·14	9·61	9·48	10·66	11·08
CaO..	0·39	0·77	0·45	0·36	0·41	1·07	0·62
H_2O..	0·77	0·73	(a)0·87	0·78	0·79	1·23	?
N ..	1·23	1·28	1·28	1·05	1·08	?	1·26

(a) A portion of this water was perhaps derived from the large amount of foreign matter contaminating the uraninite.

An examination of analyses XII. to XVI. as recalculated above hardly allows of any other conclusion than that the specimens from the above four different quarries about Moss belong to one and the same mineral species. While analysis XII. differs in some respects from Blomstrand's analysis of bröggerite, which is here reproduced in its original form and as modified by substitution of Fe_2O_3 for FeO, it simply serves to show, assuming correct analyses, that the mineral may vary in composition in the same quarry, for, as before mentioned, this is the original material from which Blomstrand made the species.

The estimation of UO_2 in the analyses of Table IV. is thoroughly to be depended on, aside from the slight deduction to be made for possible ferrous oxide, while in

Blomstrand's Bröggerite.

UO₃	..	..	..	38·82	36·31
UO₂	..	..	..	41·25	43·62
ThO₂	..	..	..	5·64	5·64
Y₂O₃	..	..	..	2·42	2·42
Ce₂O₃	..	..	..	0·38	0·38
CaO	..	..	..	0·30	0·30
PbO	..	..	..	8·41	8·41
FeO	..	..	..	1·26	Fe₂O₃ 1·40
H₂O	..	..	..	0·83	0·83
SiO₂	..	..	..	0·81	0·81
				100·12	100·12

view of the want of evidence as to the manner of filling his tubes with carbonic acid there is no guarantee that Blomstrand's figure may not be too low. Leaving out of consideration for the moment the nitrogen, it is clear in any case that the formula evolved by him from his analysis cannot be derived from No. XII.

In regard to analyses XIII. and XIV., there can exist no doubt whatever as to the identity of the material derived from Profs. Brögger and Nordenskiöld independently. A comparison of them with Lorenzen's analysis, coupled with the fact that not one of the specimens from the neighbourhood of Moss above analysed contains less than 8 per cent of earths, gives rise to the strongest possible suspicion that that analyst has overlooked thoria altogether, notwithstanding the fact that the present material is from Elvestad and Lorenzen's (*Nat Mag. f. Naturv.*, vol. xxviii., p. 249) was from Huggenäskilen.

Lorenzen's Uraninite.

UO₃	..	..	..	38·23	37·73
UO₂	..	..	..	50·42	50·89
PbO	..	..	..	9·72	9·72
FeO	..	..	..	0·25	Fe₂O₃ 0·28
CaO	..	..	..	0·21	0·21
H₂O	..	..	..	0·70	0·70
SiO₂	..	..	..	0·31	0·31
				99·84	99·84

Prof. Brögger, as quoted (*ante*), says, however, that the material sent by him is to the best of his knowledge from the same place as that analysed by Lorenzen, and this appears probable from the fact that the specimens from Huggenäskilen sent by Prof. Nordenskiöld show a totally different ratio between UO₂ and UO₃ (anal. XVI.). If it should prove that Lorenzen erred in overlooking thoria, another of Blomstrand's supports in favour of the orthouranate formula for all uraninites, including bröggerite and cleveite, is knocked away, the first being the earlier and, as shown, incorrect analysis of Branchville uraninite.

The oxygen ratios calculated for analyses XII. to XVI., counting all earths as thoria, whereby the comparison is very little affected, since the percentages of the other earths are almost alike in all analyses, are as given below, as also the ratios for Blomstrand's bröggerite calculated from the second column (see above) instead of the first in order to compare properly with the others.

It is seen that none of the analyses conform even approximately to the ratio for Blomstrand's, except that of the mineral from Huggenäskilen. A re-calculation of all on the basis of FeO for Fe₂O₃ and consequent changes in UO₂ and UO₃, and separation of the earths, would give the normal ratio 1 : 1 for Blomstrand's analysis, but

the others would differ from it more widely than in the above exhibit.

The correctness of the orthouranate formula for bröggerite itself having been invalidated by the difference between his own analysis and anal. XII. above, it is hardly worth while to discuss its applicability to the Bohemian and Saxon uraninites, of which no complete and reliable analyses seem to have been made, except perhaps the single one by Ebelmen in 1843 on Joachimsthal material, which on re-calculation by Blomstrand was found to conform to his view. No more singular example can be furnished of incorrect conclusions founded on seemingly the best of evidence. No blame can attach to Blomstrand, but it can hardly be doubted that had he been able to analyse material from more than one quarry about Moss he would have seen the impossibility of reconciling the discrepancies in composition so as to admit of the application of one general formula.

It is apparent, notwithstanding the deficiency of earths and one or two other discrepancies, that analysis XVII. was really made upon cleveite, as the label indicated. The density, too, corresponds almost exactly with that found by Nordenskiöld (*Geol. För. Förh.*, 1878, vol. iv., p. 28 ; *Zeit. f. Kryst.*, vol. iii., p. 201) and Lindström. In the latter's analysis, which is quoted below, " water and a trace of CO₂ " are given as loss on ignition, a result which under the circumstances must be considered unreliable.

The same objection applies to Hidden and Mackintosh's analysis of nivenite (*Am. Jour. Sci.*, [3] 1889, vol. xxxviii., p. 481), where it is stated plainly that the water represents loss on ignition. The analyses of clevite and nivenite are here given together with XVII. from Table IV. for convenient comparison. It may be mentioned that the 23·07 per cent of UO₂ in clevite is the mean of two results differing by nearly 1½ per cent. Taking the higher as more nearly correct than the mean, almost exact agreement with the figures of analysis XVII. for UO₂ and UO₃ is obtained.

				Nivenite.	Cleveite.	XVII.
UO₃	..	..	..	46·75	40·60	41·71
UO₂	..	..	..	19·89	23·07	24·18
ThO₂	..	..	..	7·57	4·60 ⎫	3·66
Ce₂O₃, &c.	..	..	—	2·25 ⎭	
Y₂O₃, &c.	..	..	11·22	9·99	9·76
PbO	..	..	..	10·16	10·92	10·54
Fe₂O₃	..	..	..	0·58	1·02	0·03
CaO	..	..	..	—	0·86	1·06
MgO	..	..	..	—	0·14	(a)0·33
SiO₂	..	..	..	—	—	0·90
Ign.	..	..	..	2·54	4·96	H₂O 1·23
Insol.	..	..	..	1·22	2·34	1·10
CO₂ and N ?	..	..	—	—	5·50
				99·93	100·75	100·00

(*a*) And alk.

The appearance of cleveite is at once suggestive of alteration, and, in view of the uncertainty attaching to the water determinations for both nivenite and cleveite, it is probable that they represent nearly the same stage of alteration of the same species. What this species is is pretty clearly indicated by analysis XVIII. of Table IV., where the earths are in about the same proportions and total amounts as in XVII., but the UO₃ and UO₂ stand in a very different ratio. The material for this, as before said, came from Arendal, and presumably from the precise locality of the cleveite of analysis XVII., since the pieces

					Mol. wt.	XII.		XIII. and XIV.		XV.		XVI.		Blomstrand's Bröggerite.	
UO₃	..	..	..	..	287	5·36	1	4·31	1	5·44	1	5·97	1	6·07	1
UO₂	..	..	..	..	271	5·70 ⎫		6·01 ⎫		5·26 ⎫		5·14 ⎫		5·15 ⎫	
Earths	..	..	..	..	266	0·96 ⎬ 1·37		1·21 ⎬ 1·85		1·28 ⎬ 1·33		0·98 ⎬ 1·14		1·02 ⎬ 1·11	
PbO	..	..	..	..	223	0·68 ⎭		0·73 ⎭		0·69 ⎭		0·68 ⎭		0·60 ⎭	

of felspathic rock containing them were in one package without distinguishing labels, but it was unquestionab y fresher. The extreme solubility of this material compared with the other Norwegian uraninites is shared by that of analysis XVII., by cleveite, and by nivenite, and is to be explained probably not so much by advanced decomposition as by the preponderance here of a more soluble yttrium-uranium compound. Whether or not this last Arendal material is the source whence cleveite and its American representative have been derived by alteration, as seems most probable, it is in any event a true uraninite of more basic character than any of the Norwegian thorium uraninites, and consequently conforms still less than those to the orthouranate formula.

Bohemian and Saxon Uraninite.—Nitrogen was carefully sought for in uraninite from Przibram, Joachimsthal, and Johanngeorgenstadt, using the apparatus figured (*ante*). The extremely small bulk of gas finally obtained from all of them, after cleansing with potassium hydrate, measured about 0·2 c.m.³ for Przibram and Joachimsthal, and much less for Johanngeorgenstadt, 1 grm. of mineral having been used. The above volume represents about 0·02 per cent in weight of what can hardly be anything else than nitrogen.

None of the specimens contained zirconia, thoria, or other rare earths. Owing to the uncertainty of being able to determine with any close approach to truth the proportions of UO_2 and UO_3 in the presence of sulphides, and compounds of arsenic and vanadium of unknown degree of oxidation, no quantitative analyses have been carried out, but the attempt will yet be made to solve their composition.

Discussion of Analyses.

Hitherto the analyses have been considered in groups and without special reference to the nitrogen. It has been sought to show on grounds which would be valid even without its presence that the orthouranate formula is capable of no general application to uraninite, and that in the one or two cases where it does seem to apply this agreement is probably accidental. Taking into consideration the low atomic weight of nitrogen as compared with uranium, thorium, and lead, it is plain that it must play an important part in the constitution of the molecule, and that therefore its discovery alone, without other evidence furnished by the analyses, is sufficient to invalidate entirely the practically identical formulæ of Comstock and Blomstrand.

Throughout the whole list of analyses in which nitrogen has been estimated, the most striking feature is the apparent relation between the UO_2 and the nitrogen. This is especially marked in the second table of Norwegian uraninites (Table V.), from which the rule might almost be formulated that, given either nitrogen or UO_2, the other can be found by simple calculation. The same ratio is not found in the Connecticut varieties, but if the imperfect determination of nitrogen in the Branchville mineral is to be depended on, the rule still holds that the higher the UO_2 the higher likewise is the nitrogen. The Colorado and North Carolina minerals are exceptions, but it should be remembered that the former is amorphous, like the Bohemian, and possesses the further similarity of containing no thoria, though zirconia may take its place, and the North Carolina material is so much altered that its original condition is quite unknown.

In the absence of all positive knowledge whatever as to the rôle which nitrogen plays in the mineral, it would be idle to speculate at present upon the proper position of the latter in mineral classification. Much remains to be done before this question can be elucidated, but the general direction which the work must take can be fairly indicated.

But two explanations seem possible to account for the wide differences in the oxygen ratios for UO_3 and total bases, varying as they do from 1 : 4·37 for the Branchville

material of analysis VI. to 1 : 1 for Blomstrand's brögerite, and even to a ratio indicating acidity for nivenite. Either all the others are alteration products of a mineral having the composition of the Branchville occurrence, or even of some unknown body entirely free from UO_3 ; or they are mixtures of two or more substances which need not necessarily be isomorphous, for Baumhauer's investigations have shown that even well developed crystals of smaltite and chloanthite are often mechanical mixtures. Fractional solution might throw light on this point, and the following are the results of experimentation :—

I. In one of the nitrogen estimations in Glastonbury uraninite by the original method the operation had to be discontinued before solution was complete. The undissolved residue, amounting after extraction of lead sulphate to 0·1234 grm., was found to contain 71·94 per cent UO_2, the original percentage having been 59·93.

II. 1·095 grms. were boiled for twelve hours with dilute hydrochloric acid in a flask connected with a reversed condenser. The residue was 0·9193 grm., showing that but 16 per cent had been dissolved, and it contained 64·66 per cent UO_2. The nitrogen was lost.

III. 2·012 grms., when boiled with the same hydrochloric acid for forty-two hours, afforded a residue of 1·4975, showing solution of 25·5 per cent. Its composition was—

UO_3	16·63	} All U as UO_2 82·52.	
UO_2	66·82	}	
Earths	10·81		
PbO	3·02		
N	2·67		
H_2O	(?)		
Insol.	0·37		

100·32

Here it is seen that the UO_2 has increased, and likewise the nitrogen, both in about the same proportion, but it is not clear why the earths and lead oxide should not show a greater change.

These experiments require repetition and extension to other than the Glastonbury mineral, but so far as they go they indicate that uraninite as we know it is not a single chemical substance, and that, as was to be expected in such case, the portion containing most UO_2 is the least soluble. They are not decisive as between the hypothesis of original mixture and that of mixtures resulting from alteration. In this respect the following observations are of interest :—In dilute hydrochloric acid a large piece of North Carolina uraninite falls wholly to finest powder in course of time, which would hardly happen were it one original substance in process of alteration, unless the change affected every smallest particle of the mineral simultaneously and to the same extent. Hydrofluoric acid speedily covers the faces of a bright crystal of Branchville uraninite with a network of fine cracks visible only under the glass, and soon powder can be rubbed off with the fingers.

Whatever may be the eventual conclusion, it will be found that the small amount of water afforded by all analyses must be carefully considered. Small as this amount is, in consequence of its low molecular weight as opposed to uranium, thorium, and lead, it must play an important part in the mineral as a homogeneous whole or in one of its parts if a mixture. In the latter case it will unquestionably be found to belong to the more soluble component.

It is significant that the two uraninites highest in UO_2 give the lowest water, and while it is true that the Branchville mineral appears to contain more than that from Glastonbury, this may be only apparent, for the former was simply ignited in a current of air, while the latter was fused with sodium carbonate, and it is known that the vapours from both possess an acid reaction, and

in the latter case give an increased weight to the calcium chloride tube when no alkaline carbonate is used. It is important that in all future analyses stress shall be laid upon the utmost accuracy in the water determinations, and if insoluble matter is present, it must be ascertained if possible how much, if any, of the water is to be ascribed to this source.

Before leaving this portion of the subject it is necessary to call attention to one difficulty presented by the analyses for which no satisfactory explanation yet presents itself. In the majority of cases in which all constituents have been estimated, the summation is considerably in excess of 100, and in some cases where only one or two are wanting it is evident that they would, if determined, produce a like result. Although it did not seem possible that this almost constant excess could be due to impurities from reagents, or to want of sufficient care in washing or igniting precipitates, it was determined to make an analysis on Glastonbury material with the utmost possible care, using specially prepared reagents and only platinum vessels and reducing the number of weighings to be used as the basis for the summation to a minimum. This analysis, executed partially in duplicate, is No. V. of Table I., and the excess still appears. It seems as if some one of the weighings must have been uniformly too high, but how this can be is a mystery. Efforts will still be made to find a solution. It cannot be sought in a replacement of oxygen by nitrogen in combination with uranium, like the replacement of oxygen by fluorine in many minerals, for since the nitrogen is freed as a gas by sulphuric acid, it is immaterial, so far as the summation is concerned, whether the proportions of UO_2 and UO_3 as found by titration are correct or not. A certain amount of oxygen has been used, and, assuming its correct determination, it does not alter the result whether this has been employed to oxidise a suboxide of uranium to UO_3, supposing nitrogen to have replaced a part of the oxygen in UO_2, or only in oxidising UO_2 to UO_3. In the former case the actual percentage of UO_3 in the mineral would be increased, but the oxygen consumed would be the same.

In a former notice (*Am. Journ. Sci.*, 1889, [3] vol. xxxviii., p. 329) it was mentioned that a relation appeared to subsist between the nitrogen and the UO_2, but this statement was based on two experiments which subsequent work showed to be illusory. There is certainly a relation, but not exactly such a one as was then surmised. It was found, namely, on examining the portions used for water determinations (by ignition in dry air without sodium carbonate) for UO_2 and nitrogen, that the residual amounts of these were exactly in proportion to their original percentages, showing that the loss of nitrogen kept step with the oxidation of UO_2 to UO_3. It was later found that these results were accidental, for by sufficiently long heating the nitrogen was entirely eliminated, so far as the usual tests showed.

(To be continued).

Volumetric Determination of Hydrocarbon Vapours in Coal-gas.—W. Hempel and L. M. Dennis (*Ber. Deutsch. Chem. Gesell.*).—The gas is measured in a simple gas burette over water saturated with coal-gas; it is then conveyed through a capillary tube into a gas pipette, in which it is in contact with 1 c.c. of absolute alcohol over mercury, with which it is shaken up for three minutes. The gas is then returned to the burette, taking care that no alcohol penetrates into the connecting capillary. In order to absorb the alcoholic vapour out of the remaining gas, it is again conveyed into a pipette, in which it is shaken up for three minutes with 1 c.c. of water over mercury, after which the gas is conveyed back into the burette. The difference of volume corresponds to the vapours.

OPENING UP CHROME IRON ORE BY HYDROCHLORIC ACID UNDER PRESSURE.

By PAUL JANNASCH and HANS VOGTHERR.

MY recently published method of opening up silicates by means of strong hydrochloric acid under pressure in a special platinum apparatus, has been since applied, in concert with H. Vogtherr, to an extensive series of minerals with great success. We have succeeded in completely opening up silicates, such as garnet (pyrope of Meronitz and Arendal, &c.), also black horn-blende (from Granatilla and from Schima), also cerite, so as to be quite suitable for the purpose of an accurate quantitative analysis.

The more detailed results, as well as the different modifications in the execution of the process, will be published in a future communication. In the present short communication we wish in the first place to direct attention to the energetic action of concentrated hydrochloric acid under pressure upon chrome iron ore, which is well known to be very refractory under the common method of opening up by fusion. It is perfectly opened up by hydrochloric acid at 250°, which will greatly facilitate the accurate and complete analysis of the many important deposits of this mineral. The opening up of the mineral is effected as follows:—

I.—*Chrome Iron Ore from Baltimore.*

The ore, in fine powder, was mixed with 2 grms. sal-ammoniac and 10 c.c. of hydrochloric acid (4 vols. acid at 1·119 specific gravity to 1 vol. water), sealed up in a tube of potash-glass and heated for 8—10 hours to 275—290°. The acid employed had been previously saturated with ammonium chloride by shaking up with the latter salt. The quantity of ore taken was 1·0426 grms. The silica, = 0·0194 grm. = 1·86 per cent, was volatilised by heating on the water-bath with hydrofluoric and sulphuric acids; the residual sulphuric acid was evaporated on the air-bath, and the residue was ignited and weighed. It amounted to 0·0018 grm. = 0·17 per cent.

II.—*Chrome Iron Ore from Frankenstein in Silesia, and* III.—*Chrome Iron Ore from Orsova.*

Both these specimens were treated in a similar manner.

In practice, if it is merely required to determine the percentage of chrome in a specimen, the author's platinum apparatus may be dispensed with, and the opening up may be effected in a sealed tube.—*Ber. d. Deutsch. Chem. Gesell.*, vol. xxiv., p. 3206.

A Spectro-Colorimeter.—D'Arsonval (*Séances Soc. Franc. de Phys.*).—In this instrument the eye-piece of an ordinary Dubosq colorimeter is replaced by a small direct vision spectroscope, the slit of which is fixed vertically to the line separating the two halves of the field of vision. If the liquid under examination is placed in one of the tubes and the standard of comparison in the other, and if the substance produces sufficiently characteristic absorption-phenomena, a given constituent can be recognised even in a mixture of bodies of different colours. The same author describes (*ibidem*) a differential spectrometer without polarisation. The rays coming from the sources of light to be compared are thrown upon two parallel tubes closed by two similar objectives, and placed before a spectrum apparatus. The light of each source is thrown upon one-half of the slit by two pairs each of two total reflective prisms. In order to vary in a measurable manner the luminosity of the two spectra, which appear superimposed, a sliding screen is placed before the two object-glasses, which cuts off the light differently, according to its position.

NEW METHOD FOR THE ANALYSIS OF TIN ORES, AND FOR THE SEPARATION OF COPPER AND CADMIUM.*

By J. S. C. WELLS, Ph.D.

TIN ORE.

THE methods for the analysis of tin ores are so tedious and unsatisfactory that I was led, some time ago, to try and discover some simpler way of decomposing the ore; that being the chief difficulty in all the old methods.

In my first experiments, fusing the ore with borax was tried, and although this was found to effect the desired result, as far as the decomposition of the ore, still it introduced other difficulties that caused me to give it up.

The borax, at the high temperature of the fusion, attacked the platinum of the crucible to such an extent that it became necessary to separate the platinum from the tin. Boracic acid, as was to be expected, acted the same as borax. The idea then occurred to me that the ore might possibly be reduced in the same way as the artificial oxide, *i.e.*, by means of nascent hydrogen. On trying the experiment, I found that in this way the tin contained in the ore could easily be obtained in the metallic state. My first tests were made as follows:— About 1 grm. of the finely pulverised ore was placed in a large test-tube with a few pieces of zinc and some dilute hydrochloric acid. The first trials were made on an ore from Cornwall, and it was found to be very easily reduced. A sample of Durango ore, consisting of nearly pure cassiterite, was then tried, but the reduction did not take place as readily as with the ore from Cornwall; the reduction of the latter was nearly complete at the end of an hour, whilst the former at the end of three hours showed little change. I then added a piece of platinum with the zinc and acid, and found the result to be very satisfactory, the ore being quickly reduced. Heating the test to boiling was also found to aid the reaction. The addition of the platinum also facilitates very much the subsequent solution of the reduced tin in hydrochloric acid, tin alone dissolving but slowly in the acid.

It is advisable to shake the test frequently during the reaction, so as to keep the ore in contact with the zinc and platinum. If this is not done, the ore settles to the bottom and the reduction takes place very slowly, if at all.

As soon as the decomposition of the ore appears to be complete, the remaining zinc and the reduced tin are dissolved in hydrochloric acid and filtered from any undecomposed ore or gangue. This residue should again be tested in the same way, with fresh zinc, platinum, and hydrochloric acid, to see if all the tin has been extracted by the first operation. After the tin has been obtained as chloride, it can, of course, be determined by any of the usual methods.

Instead of dissolving in hydrochloric acid, the tin might be dissolved in ferric chloride, after removal of the excess of zinc, and then determined volumetrically. The metal, being in such a finely divided state, would be very easily soluble in this reagent.

SEPARATION OF COPPER AND CADMIUM.

I find that copper and cadmium may be easily separated by the following method:—

To the neutral solution containing these metals (ammonia salts must not be present) add sodium thiosulphate (hyposulphite) until the solution becomes colourless, then add sodium carbonate, and the cadmium will be precipitated as carbonate (white); filter, and to the filtrate add HCl, and boil, and the copper will be precipitated as sulphide. To use this method in the ordinary course of analysis, the solution, after removal of the bismuth, would

have to be evaporated to dryness and ignited so as to remove all ammonia salts.

ON NEW QUANTITATIVE SEPARATIONS OF MANGANESE AND NICKEL, MANGANESE AND COBALT, AND OF MANGANESE, NICKEL AND COBALT.

By PAUL JANNASCH and CARL J. FRANZEK.

SOME time ago one of the present writers, in concert with Mr. McGregory, succeeded in ascertaining and laying down those conditions under which manganese and zinc may be very conveniently and exactly separated by means of hydrogen peroxide in a strongly ammoniacal solution, and in presence of very much ammonium chloride. We are now in a position to state that the separation of manganese and nickel can be effected under the same conditions and with the same accuracy as that of manganese and zinc.

In view of these experimental facts we hoped to separate manganese and cobalt in the same or in an analogous manner. But our analyses soon showed the impossibility of a quantitative separation of the two metals in the manner adopted, for all our experiments failed by reason of the marked obstinacy with which very considerable quantities of cobalt (on the average several per cents) adhered to the manganese hydroperoxide, so that even precipitations of the manganese several times repeated proved quite unsatisfactory.

After a long series of the most different modifications of the experimental conditions, we found the solution of the double (potassic) cyanide of the metals an excellent means for the quantitative separation of manganese and cobalt. From such a solution hydrogen peroxide throws down manganese absolutely free from cobalt. The behaviour of a solution of potassium-manganese nickel cyanide is quite similar, and, as it might be expected, the corresponding solution of all the three metals concerned. But in the execution of this new process for separating manganese, nickel, and cobalt, certain definite proportions of the reagents to be used are absolutely necessary, as is also the attention to certain precautions, the full description of which will form the subject of a future communication. — *Berichte der Deutsch. Chem. Gesell.*, vol. xxiv., p. 3204.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

November 19th, 1891.

SIR HENRY ROSCOE, F.R.S., in the Chair.

CERTIFICATES were read for the first time in favour of Messrs. Hugh Brown Collins, West Balgray, Glasgow; Albert Henry Luckett, Brighton College, Brighton; James Hill Millar, 13, Waterloo Road, Wolverhampton; James Alexander Schofield, University of Sydney, New South Wales; Morris William Trewers, 2, Phillimore Gardens, Kensington, W.; Hugh Woods, 11, Archway Road, Highgate, N.

The following papers were read:—

67. "*Iron Carbonyl.*" By LUDWIG MOND, F.R.S., and Dr. LANGER.

The authors have isolated two compounds of iron with carbon monoxide, represented by the formulæ $Fe(CO)_5$ and $Fe_2(CO)_7$, for which they propose the names ferropentacarbonyl and diferroheptacarbonyl.

The ferropentacarbonyl is obtained by exposing finely divided iron in an atmosphere of carbon monoxide at the ordinary temperature during about twenty-four hours, and then heating to about 120°. A small quantity (about 1 grm. from 100 grms. of iron) of an amber-coloured liquid is thus obtained, of the relative density 1·4666, which solidifies below −21°, forming acicular, yellowish crystals. The compound distils unchanged at 102·8°, the vapour having a density of 6·5, that corresponding to the formula $Fe(CO)_5$ being 6·7. It is not acted on by dilute acids; nitric acid, chlorine, and bromine destroy it; alcoholic solutions of alkalis readily dissolve it, and form red-coloured solutions, which rapidly change in contact with air, but from which, as yet, no definite compounds have been obtained.

Diferroheptacarbonyl is obtained by exposing the liquid ferropentacarbonyl to light. It separates in gold-coloured crystals, carbon monoxide being liberated. The crystals are almost insoluble in all ordinary solvents; they are not volatile, but on heating to 80° they are decomposed into iron, ferropentacarbonyl, and carbon monoxide. The crystals are not changed by dilute acids, but are readily acted on by nitric acid, bromine, and chlorine. Alcoholic potash dissolves them, forming a red solution, very similar to the solution of the ferropentacarbonyl.

A lecture was then delivered on—

" *Colour-Photometry.*" By Captain ABNEY, C.B., D.C.L., F.R.S.

Colour has been usually made the subject of reference to empiric and variable standards, a practice which affords results useless for future reference, and only suitable for present immediate wants. What is required is a reference to numbers which are on some standard scale that can easily be reproduced.

According to the lecturer, *the colour of a body, when viewed in a light of standard quality, is known when* (a) *its luminosity,* (b) *its hue, and* (c) *its purity, or the extent to which it is freed from admixture with white light, are known and expressed by numbers.*

The luminosity of a colour can be given in absolute number by referring it to the standard of white. Thus, if white light fall on a coloured surface and on a surface of some standard white, the luminosity of the former may be expressed in terms of that of the light. It may appear difficult to compare the brightness of two such surfaces, but as a fact, the comparison is easily accomplished by causing the light falling on the white surface to be rapidly alternately made brighter and darker than that falling on the coloured surface. This can be done by interposing in the beam falling on the white surface rotating sectors with apertures which open and close *at will* during rotation. The point of equal luminosity can be found by this plan within 1 per cent. Experiments exemplifying the method were made, the brightness of an orange and of a blue pigment being compared with that of a zinc oxide surface which the author uses as standard white. It was also shown by sending the beams through a trough containing water in which mucin was suspended in minute particles, that the relation only held good for the particular light in which it was measured. Hence the necessity for using a standard light.

The luminosity of the light transmitted through coloured translucent bodies was also measured, and the same necessity shown for the use of a standard light.

The standard light recommended was that from the crater of the positive pole of the electric light when high illumination was required, or from a petroleum lamp when the illumination need not be so intense.

The method of measuring the luminosity of *light coming through translucent bodies* was also shown. A white oblong of paper was placed on a blackened card, a square which occupied half this oblong being pierced in the card, and thus half could be illuminated from the back of the card, and the other half by light from the front by placing a rod in the path of the beam to cast a shadow

on the first half. The translucent substance was placed close behind the aperture in the card, and the light illuminating the paper, after passage through the translucent medium, was measured by altering the illumination of the other half lighted from the front.

The luminosity of the pure spectrum colours may be measured by what the author calls the colour patch apparatus, which is described in the *Phil. Trans.*, 1886, and in his work on " Colour Measurement and Mixture." It essentially consists of a collimator, two prisms, a lens, and a camera, on the screen of which a spectrum is brought to a focus. This screen is removed for experiments, and a collecting lens used to re-combine the spectrum, and to form an image of the last surface of the second prism on a screen some four feet off. A slide with a slit passed through the spectrum causes the white patch to become a colour patch of monochromatic light due to the particular ray traversing the spectrum slit. The white light with which the colour is obtained is compared from the light coming through the collimator and reflected from the first surface of the first prism; by means of a mirror and lens, it forms a patch equal in size to, and which can be caused to overlap, the coloured patch, or to lie alongside of it. In the first case, a rod placed in the path casts two shadows, one of which is illuminated by the colour and the other by the white light; rotating sectors in the path of the latter allow the luminosity to be compared. The light used in the electric light, an image of the crater of the positive pole being formed on the slit of the collimator.

The luminosity of a colour is not the same when viewed from all parts of the eye. The centre of the eye is that with which observations are usually made; hence the luminosity should be measured with that part of the retina, and it is advisable that no more than 6° of angular measure from the eye should be compared.

The audience were enabled to see the difference in luminosity of a colour which was of equal brightness to a certain white when viewed centrally, by shifting the axis of the eye so that the image was received on the retina some 10° away from the centre.

The action of the yellow spot was then alluded to.

The luminosity of any pigment on paper can be found by rotating it with two of the three colours : red, emerald green, and ultramarine.

These three make a grey which matches a grey formed of black and white. If the luminosity of the three have been accurately determined, by substituting the pigment whose luminosity is required for one of them, another grey can be formed to match a grey consisting of black and white. After measuring the angular aperture of the sectors, the luminosity is determined by calculation; the result is found to agree with the measurement made by the direct method. This is one of the many proofs that the measure of luminosity obtained in the manner described is correct, and not a mere accident.

The colour of a pigment can be referred to the spectrum colours by measuring the absorption. In the case of transparent bodies, this is best done by using a double-image prism at the end of the collimator so as to form two spectra on the camera screen. By adjustment, these may be caused to be so exactly one over the other, that the same colour will pass through a slit in them. After emergence from the slit, the rays from the top spectrum are diverted by a right-angle prism, and caught by another which sends them through a lens on to the screen, forming a patch. Another patch as usual is formed by the rays from the bottom spectrum. By placing the transparent body in the path of one of these rays, the absorption can be measured by equalising the brightness of the patches by the sectors and noting the apertures. The absorption of pigments can be measured in the same way by causing one patch to fall on the coloured surface and the other on the standard white.

To measure the absorption of pigments an easy plan is to rotate black and white sectors together with variations

in the amount of white, and to cause the colour patch to fall partly on them and partly on the pigment. The colour is varied till it is seen that the grey disc and the pigment reflect the same amount of light.

By both these plans, templates can be cut out, which, when rotated in the spectrum, give the exact colour of the pigment on the screen ; hence this is a reduction of the true colour to absolute numbers, since the colour can be reproduced from a reference to a note book. It is to be remarked that the measures are unaffected by any defect in the eye of the observer, or by the kind of light in which they were effected.

The mixture in varying proportions of red, green, and violet of the spectrum makes white. This was shown by placing three slits in standard positions in the spectrum, and altering their apertures till a match was made with a patch of white light alongside.

Any other colour can be matched by the mixture of the same three colours, as was shown in matching green, blue, and brown papers.

Since three colours will make white, and the same three colours will make a match with an impure colour, every colour in nature can evidently be matched by mixing not more than two of these colours with a certain proportion of white light ; and if these colours be red and green, or green and violet, the colour can be matched by one spectrum colour and white light, since there is some intermediate colour which has the same hue as the mixture of these two colours. Hence any colour, except purple, can be referred to some spectrum colour, together with a certain proportion of white light. In the case of purple, the colour may be expressed as white light, from which the complementary colour is eliminated. *Hence any colour whatever may be expressed in terms of white light and one spectrum colour, the latter in wave-lengths, and the former in percentage of luminosity.*

This was shown to be the case by interposing between the silvered mirror which reflected the light coming from the first prism, and which formed the white comparison patch, a plain glass mirror which reflected a small percentage of the light on to the colour patch, the amount of which could be regulated by sectors. Brown paper was placed in the white patch, and the spectrum colour was changed and mixed with the white light till the same colour was obtained. The scale of the instrument told the wave-length, and, by interposing a rod in the path of beams, the proportional luminosities of the spectrum colour and of the white light were determined. A similar match was made by light going through signal-green glass, and the complementary colour of the light passing through permanganate was determined.

Light coming through properly picked specimens of red, blue, and green glass, and overlapping, may also be made to match a colour.

The three glasses covered a square lens, and formed an image on a screen of a circular patch of white light coming through ground glass on a screen. Colours were placed on a white beam alongside, and by altering the amount of the coloured glasses exposed, matches were made.

If the dominant wave-lengths of the colour of these three glasses be known, and also the amount of white light mixed with it, these measures can be noted in terms of these three glasses ; and, further, it is possible, by mixing the light coming through the three glasses in various proportions, to obtain a spectrum colour mixed with white light for each such mixture. Hence this is a substitute for the spectrum itself. To show this, three similar glasses were placed over apertures suitably cut in a circular card ; and, by causing these to rotate in front of an illuminated slit, a sham spectrum was thrown on the screen in which every colour was present.

Any colour can be reproduced with three rotating sectors of red, green, and blue, when certain proportions of white or black, or both, are mixed with one or other. If the dominant wave-lengths and the proportion of white light

mixed are known of each such colour, the pigment whose colour is to be determined can be expressed in numbers as before, and in terms of spectrum colours if desired.* This was shown by matching brown paper with red, blue, and green, a little white and black being mixed with the brown.

The importance of using some uniform light was insisted upon throughout, slight deviations in the experiments demonstrating this.

In conclusion, Captain ABNEY claimed to have demonstrated that the reference of colour to numbers was not only possible but easy, and that, to chemists especially, the application was one of almost capital importance. Everyone could do it, and the lecturer had an instrument on the stocks which was not so cumbersome as that shown, but which would answer all purposes, he hoped, when complete.

ROYAL INSTITUTION OF GREAT BRITAIN.

General Monthly Meeting, Monday, December 7, 1891.

SIR JAMES CRICHTON BROWNE, M.D., LL.D., F.R.S., Treasurer and Vice-President, in the Chair.

THE following were elected Members of the Royal Institution :— Lorentz Albert Groth ; John Imray, M.A., M.Inst.C.E. ; George Stillingfleet Johnson, F.C.S. ; John List, M.Inst.C.E. ; Mrs. Douglas Powell ; James Shand, M.Inst.C.E. ; Mrs. Thomas Threlfall.

The Special Thanks of the Members were returned for donations from Professor Dewar (for structural alterations) ; from Mr. Ludwig Mond (for new pressure pump).

The Chairman reported that the late Mr. J. P. Stocker had bequeathed £100 to the Royal Institution.

The Presents received since the last meeting were laid on the table and the thanks of the Members returned for the same.

CORRESPONDENCE.

THE DETERMINATION OF THALLIUM.

To the Editor of the Chemical News.

SIR,—In the number of your journal issued November 13th there is an article by M. Baubigny on the "Determination of Thallium," from which it appears that the author has completely overlooked my experiments on that subject, published in the *Journ. Anal. Chem.*, 1888, page 243. (See also *Zeit. fur Anal. Chem.*, 1891, 342.) In my investigations I determined the solubility of thallous iodide under various conditions, and reached conclusions not essentially different from those of M. Baubigny. The collection and weighing of the precipitate on a Gooch filter, which I recommend, is certainly far more accurate and convenient than is the method followed by this chemist.

I will add here that the Gooch filter, whose merits do not seem to be fully understood and appreciated abroad, is described in the CHEMICAL NEWS of May 3rd, 1878.— I am, &c.,

JOHN H. LONG.

Chicago, Nov. 24, 1891.

The Use of the Pendulum as a Balance.—K. Fuchs (*Zeit. Phys. Chemie*).—The centre of gravity of a pendulum rod about 2 d.m. in length, lies rather above the fulcrum. Check-pieces on both sides of the top prevent the rod from turning over when not loaded. The lower end carries a basket to receive the body to be weighed, and so many weights that the centre of gravity falls somewhat below the knife-edge support, whereby the rod is able to make slow oscillations of 5 — 10 seconds duration. The weight of the body can be calculated from the time observed according to a method given.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxiii., No. 21, November 23, 1891.

Preparation and Properties of the Boron Phosphides.—Henri Moissan.—The author, taking boron phosphoiodide as his point of departure, has obtained two boron phosphides. One of these, PB, combines with incandescence with monohydrated nitric acid, and takes fire in the cold if immersed in chlorine. The other compound, P_3B_5, is much more stable, and is not decomposed in the cold by these two reagents.

Mechanical Determination of the Position of the Atoms of Hydrogen in Organic Compounds.—G. Hinrichs.—The author concludes that the primitive form, CH_4, of organic compounds cannot be a tetrahedron, of which the atoms of hydrogen form the corners whilst the atom of hydrogen is the centre. On the contrary, the four atoms of hydrogen of CH_4 form the angles of a square above the square surface of the atom of carbon.

On Aniline Black in Dyeing by the Dry Way.—S. Grawitz.—The writer proposes to add to Lightfoot's formula for aniline blacks alkaline or earthy alkaline bases in the state of organic salts, such as acetates with or without an excess of organic acid. This black is said not to smear off.

On a Codeine Violet.—P. Cazeneuve.—This compound, to which the author assigns the formula—

$$N \begin{cases} C_6H_4N(CH_3)_2 \\ C_{17}H_{18}NO_4(CH)_3' \end{cases}$$

dyes wool, silk, and gun-cotton, like morphine violet. Light slightly affects the colour. The yield of the product is small.

The Distribution of Saccharine Matters in the Different Parts of Boletus Edulis.—Em. Bourquelet.—Trehalose is chiefly found at the foot of the fungus. Glucose exists in a much smaller proportion. Neither of these sugars is present in the hymenophore.

Moniteur Scientifique, Quesneville.
Series 4, Vol. iv., Part 2, No. 588.

Schmidt's Process for Converting Oleic Acid into Solid Fatty Acids (*Monatshefte für Chemie*).—The methods of conversion founded on the action of nitrous acid, of chlorine, bromine, and iodine, or of melting potassa, are not economical, and sometimes too delicate for industrial use. Schmidt heats 10 parts of oleic acid to 180° with 1 part of zinc chloride. The reaction is complete when a drop of liquid taken from the melted mass and boiled in a test-tube with diluted hydrochloric acid solidifies on cooling. The whole is then dissolved in the same dilute acid, boiled by passing a jet of steam into the liquid, the aqueous portion is removed by decantation, and this operation is repeated as long as the acid extract still contains zinc. The product is then washed with water and distilled in superheated steam with an ordinary rectifier. The operation is completed by removing any unconverted oleic acid by pressure or by centifrugal action.

Specific Weights of Certain Fats and Oils.—C. A. Crampton.—(From the *Amer. Chem. Jour.*).

Characters of Castor Oil.—H. Gilbert (*Chem. Zeit.*).—Castor-oil should have a specific gravity of 0·950—0·970; it becomes turbid at 0°, with a separation of crystalline flakes; at lower temperatures it takes the consistence of butter, and mixes in all proportions with alcohol and acetic acid. A mixture of 3 parts castor-oil, 3 parts carbon bisulphide, and 2 parts sulphuric acid

should not take a brown colour. A castor-oil which becomes turbid with petroleum benzene, and gives a clear solution with 5 vols. of alcohol at 90°, may be considered as pure. These characters serve to detect the presence of extraneous fatty oils in castor-oil, but not that of resin oil. The latter has a specific gravity of 0·96—0·99, and is soluble in alcohol and acetic acid. On saponifying the oil with soda-lye, shaking the aqueous solution with ether, and expelling the latter by distillation, there remains, if resin oil be present, a residue having all the properties of resin-oil. Pure castor-oil, if shaken up with an equal weight of nitric acid at 1·31, turned slightly brown, whilst the acid remained colourless. Resin oil, if treated in the same manner, becomes almost black, whilst the acid turns of a brownish yellow.

Action of Chlorine upon Hæmatoxyline, and on the Extractive Matter of Logwood.—W. McFarlane and P. S. Clarkson.—(From the *Jour. Frank. Inst.*).

Manufacture of Colourless Tannin.—A. Villon.—(From the *Bulletin de la Soc. Chimique.*

Chemical Section of the Industrial Society of Mulhouse.—A "sealed paper" deposited in 1880 by Zurchers, of Cernay, asserts that the authors have obtained aniline black by treating a salt of aniline at a gentle heat with a solution of ammoniacal copper sulphate. Henri Schmidt sent in a paper accompanied with swatches, illustrating a new process of discharging chrome-colours before their development by steaming. A colour of chrome, gallocyanine, alizarin blue, &c., is padded upon the cloth. There is then printed on a discharge consisting of red prussiate, an alkaline chlorate, and magnesium carbonate, and the pieces are steamed, producing a white design. To this discharge is added any albumen colour to produce coloured discharges. M. Prud'homme has noticed that the solubility of tartar emetic in common salt is due to the fact that these two salts form a molecular combination, containing 1 mol. tartar emetic to 4 mols. sodium chloride. This combination renders it possible to produce a colour which is at once very concentrated and soluble, and which may be prevented from running by adding a larger proportion of tannin. M. Jacquet has observed that soap-baths soiled by aniline colours may be restored by adding a certain quantity of antimony tannate, which precipitates the aniline colour as an insoluble lake.

MISCELLANEOUS.

Royal Institution.—The following are the Lecture Arrangements before Easter :— Professor John G. McKendrick, six Christmas Lectures to Juveniles, on Life in Motion, or the Animal Machine ; Professor Victor Horsley, twelve lectures on The Structure and Functions of the Nervous System (the Brain) ; Mr. A. S. Murray, three lectures on Some Aspects of Greek Sculpture in Relief ; Professor E. Ray Lankester, three lectures on Some Recent Biological Discoveries ; Professor W. P. Ker, three lectures on The Progress of Romance in the Middle Ages ; Dr. B. Arthur Whitelegge, three lectures on Epidemic Waves ; Professor J. A. Fleming, three lectures on The Induction Coil and Transformer ; The Right Hon. Lord Rayleigh, six lectures on Matter—at Rest and in Motion ; Professor J. F. Bridge, three lectures on Dramatic Music, from Shakspere to Dryden (the Play, the Masque, and the Opera), with illustrations. The Friday Evening Meetings will begin on January 22nd, when a Discourse will be given by the Right Hon. Lord Rayleigh on The Composition of Water ; succeeding Discourses will probably be given by Sir George Douglas, Bart. ; Professor Roberts-Austen, C.B. ; Mr. G. J. Symons ; Professor Percy F. Frankland ; Sir David Salomons, Bart. ; Professor L. C. Miall ; Professor Oliver Lodge, Mr. George du Maurier ; Mr. John Evans ; Mr. F. T. Piggott ; Professor W. E. Ayrton, and other gentlemen.

MEETINGS FOR THE WEEK.

MONDAY, 14th.—Society of Arts, 8. " The Pigments and Vehicles of the Old Masters," by A. P. Laurie, M.A.
—— Medical, 8.30.
TUESDAY, 15th.—Institute of Civil Engineers, 8.
—— Pathological, 8.30.
WEDNESDAY, 16th.—Society of Arts, 8. " Typological Museums, as Exemplified by the Pitt Rivers Museum at Oxford." by General Pitt Rivers.
—— Meteorological, 7.
—— Microscopical, 8.
THURSDAY, 17th.—Royal, 4.30.
—— Chemical, 8. "The Composition of Cooked Vegetables," by Miss K. Williams. " On some Metallic Hydrosulphides," by S. E. Linder and H. Picton. " On the Physical Constitution of some Solutions of Insoluble Sulphides," by H. Picton. " Solution and Pseudo-Solution," by H. Picton and S. E. Linder. " The Change Proceeding in Acidified Solutions of Sodium Thiosulphate when the Products are Retained Within the System," and " The Action of Sulphurous Acid on Flowers of Sulphur," by Dr. A. Colefax. " The α and β Modifications of Chlorobenzene Hexachloride." by Dr. Matthews. " Camphrone, a Product of the Action of Dehydrating Agents on Camphor," by Drs. Armstrong and Kipping. " Studies on the Dibromonaphthalenes," by Dr. Armstrong and Mr. Rossiter.
FRIDAY, 18th.—Physical. " On Interference with Alternating Currents," by Mr. H. Kilgour.
—— Quekett Club, 8.

TO CORRESPONDENTS.

Saponification of Beef Fat.—We have received several letters on this and the allied subject of the Saponification of Butter. As, however, the discussion is losing its scientific character and becoming too personal to be of general interest, as no new facts of importance seem to be forthcoming, and as the correspondence cannot go on for an indefinite time, we shall ask our correspondents' pardon for closing the discussion.—*Ed. C. N.*

THE CHEMICAL NEWS.

VOL. LXIV., No. 1673

THE VALUATION OF COAL FOR USE IN STEAM BOILERS.

By THOMAS T. P. BRUCE WARREN.

THE evaporative power of a substance, when burnt under the most favourable circumstances, affords a tolerably accurate method of estimating its intrinsic value as a fuel. Evaporative power is taken as being the quantity of water lost by evaporation at 212° F. in a given time per unit weight of fuel, say, one pound, the initial temperature of the water being 60° F.; the barometric column being normal.

In carrying out the principle for the actual generation of steam in a steam boiler so as to obtain comparative results for different kinds of coal, we have a variety of conditions to contend with. The same coal may be burnt in a furnace constructed as perfectly as possible with respect to area of grate, draught of air, flues, and chimney, and still yield results which vary from those obtained with the same coal burnt under another boiler, the setting, &c., of which is practically the same as in the other case.

Priming and the escape of aqueous vapour with the steam, introduce elements of uncertainty. Hence, it is usual to take the average consumption of coal corresponding to an ordinary day's work; assuming, of course, that the consumption of steam is as near as possible uniform, and the personal equation of the fireman, as far as this function is admissible, beyond reproach. The state of the boiler, as regards fur or scale, sooty deposit, &c., even if the supply of water be accurately measured, will materially affect the result.

Mechanical stokers and mechanical shifting fire-bars will eliminate the variations introduced by hand firing and the occasional opening of the furnace doors to clean the bars. So far, the average value of different kinds of coal for generating steam at a given pressure may be taken as practically near enough.

If we estimate the chlorine per gallon in a boiler when filled to its working level, and again after two or three hours' run, the water evaporated can easily be ascertained, irrespective of spasmodic demand or lull in steam supply. By estimating the chlorine from time to time, we get a far better idea of what a boiler is doing.

We have first to ascertain the chlorine, in grms. per gallon, in the feed water, and dividing the quantity of chlorine found in the boiler water, after a few hours' run, we get a ratio for the number of gallons evaporated; multiplying the number of gallons contained in the boiler at its working level by this ratio, we get the number of gallons evaporated or concentrated to the original water level.

As the chlorides in water are all soluble, and by keeping the water slightly alkaline, so as to avoid loss of chlorine, we have an accurate and trustworthy method of finding out what a given weight of fuel has driven off in steam. Loss of chlorine and priming are the only elements likely to disturb the reliability of the result. The blow-off cock should not be used whilst these experiments are in hand. Water thickened by evaporation should be avoided by filling the boiler with fresh water on starting.

Apart from the valuation of fuel, the information thus obtained will give a very accurate idea of the state of different boilers as regards scale or fur, setting, draught, &c.

Let C be the chlorine in grains per gallon of the feed water, and let C′ be the chlorine found after a certain number of hours' run; let G be the number of gallons in the boiler to the working level, then—

$$\left(\frac{C'}{C} \times G\right) - G = $$

number of gallons evaporated.

The ratio $\frac{C'}{C}$ should be nearly constant for the same construction and capacity of boiler when worked for the same number of hours and generating the same quantity of steam, but if the steam be generated faster, we may conclude that the conditions for evaporation are more favourable and *vice versâ*. If the boilers are equally free from scale, and the generation of steam unequal, it will generally be found that the draught is better in one case than in another, or the escape of steam is unequal.

It is not uncommon to find in a set of boilers working together that $\frac{C'}{C}$ is by no means uniform for each boiler; hence the practice of blowing off or emptying after a stated period of working may be wasteful or dangerous. It is far better to be guided by a reliable hydrometer, and to blow off when the water attains a certain density. If the feed water be evaporated to any given fraction of its original bulk, and the corresponding density taken, we can determine the degree of concentration corresponding to the diminished bulk, and as this can be carried out by any one not accustomed to chlorine determinations, there is no reason why any steam-user should not have some *tolerably* accurate idea of the concentration taking place in a steam boiler.

Taking density instead of chlorine, we may write

$$\left(\frac{D' - 1}{D - 1} \times G\right) - G = \text{number of gallons evaporated.}$$

In this case, D is found by experiment, by first boiling the water, so as to throw out of solution what would be thrown out in the boiler, then making up with distilled water the loss on evaporation. In this formula the specific gravity of pure water = 1.

Let D be the initial density, and D′ the density at the end of time, T; then D′ − D is the increment of density corresponding to T, and $\{(D' - D)n\} + D$ will be the density at end of n times T.

The experimental verification may be simplified by taking a given volume of water, say five gallons, and evaporating to one pint or less, making up to one pint with distilled water; when cooled to 60° F. the specific gravity is taken, which corresponds to a concentration of 40 to 1. We then mix the above pint with one pint of feed water; the specific gravity of the mixture corresponds to a concentration of 20 to 1; by mixing this again with an equal volume of feed water we have a concentration of 10 to 1. The dilutions may be varied so as to give as many degrees of concentration as we please.

In this way we can see at once what our fuel is doing, and can check the results as often as we please without any interruption to the usual methods of valuation.

I may remark that the water from a boiler containing saline scale would vitiate the result in either case; thus, the salt dissolved out with boiling would give too high a result in the chlorine estimation, and also in density. The information thus gained would be very useful, as a steam-user would know that he had accumulated salt in his scale, and would blow off more frequently, so as to get rid of it.

On Nitrosulphobenzoic Acid and its Salts, $C_6H_3(COOH)(SO_3H)NO_2(1.2.4)$.— M. Hausser.—The author has previously mentioned the curious fact that the nitrosulphonic acids of benzene and toluene displace sulphuric acid from some of its salts. The nitrosulphobenzoic acid possesses this property in a more striking degree. The author has obtained and examined the dipotassium, monopotassium, and lead salts of the acid.— *Bull. Soc. Chim. Paris*, vi., No. 6.

NITROHYDRIC ACID.*

By TH. CURTIUS.

THE investigations on azoimidic acid have been delayed by a serious accident which occurred to one of his pupils whilst preparing the anhydrous acid. The immediate object is to find methods of obtaining this remarkable substance and its compounds without danger,—at least, those compounds the manipulation of which is not perilous. Such are above all the ammonium salt and the diammonium salts of nitrohydric acid, N_4H_4, N_5H_5, and N_8H_6; further, the salts of nitrohydric acid with the metals of the alkalis and the alkaline ear hs.

The methods had to be selected so that the preparation of the free acid was dispensed with under all circumstances. This end was reached in the following manner.

Formation of Nitrogen-Alkaline Metals.

1. From the nitroso-hydrazines, or from the azoimides by the spontaneous splitting off of water by the action of alkalies in an alcoholic solution.

2. From a quite new class of organic compounds which contain three atoms of nitrogen as an open, non-ramified chain, and which are to be regarded as derivatives of hydronitrogen, $NH_2 - N = NH$, analogous to the hydro carbon propylene, $CH_3 - CH = CH_2$.

Preparation of Sodium-Nitrogen from Benzoylazoimide.

According to the researches of Curtius and Struve, benzoic ether is converted almost quantitatively into benzoylhydrazine, $C_6H_5CONHNH_2$, by hydrazine-hydrate, according to the equation—

$$C_6H_5CO_2.R + N_2H_4, H_2O = C_6H_5CO.NHNH_2 + + ROH + H_2O.$$
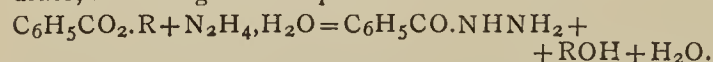
From benzoylhydrazin there is formed, as the author has previously stated, benzoylazoimide, $C_6H_5CON_3$, by the action of sodium nitrite and glacial acetic acid according to the equation—

$$C_6H_5CONHNH_2 = C_6H_5CON_3 + 2H_2O.$$
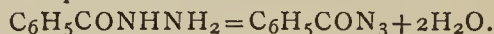
Benzoylazoimide is dissolved in an equal weight of absolute alcohol, to which is added an atom of sodium dissolved in a little absolute alcohol, and the mixture is digested for some hours on the water-bath. There are formed benzoic ether and nitrogen.—sodium according to the equation—

$$C_6H_5CON_3 + C_2H_5ONa = C_6H_5CO_2C_2H_5 + N_3Na.$$
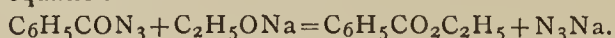
On the addition of ether the sodium compound falls down almost in a theoretical proportion after a portion has already crystallised out the alcoholic solution on cooling. The filtrate is distilled, and thus almost the calculated quantity of benzoic ether is recovered, and may be converted into the initial material benzoyl hydrazin. The nitrogen-sodium thus obtained is pure.

Preparation of Nitrogen Ammonium from the so-called Nitrosohippurylhydrazine.

Quite as convenient is the preparation of the nitrohydric salts from the product of the reaction of nitrous acid upon hippurylhydrazine. The substance was first regarded as nitroso-hippurylhydrazine, but it is a diazo-compound of the composition—

$$C_6H_5CONHCH_2CO.NH - N = N.OH.$$
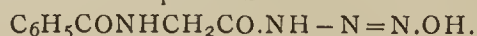
This substance cannot be converted into hippuryl-azoimide with a splitting off of water; but if dissolved in alcohol, and the liquid is saturated with gaseous ammonia, it is resolved quantitatively into hippuramide and nitrogen-ammonium according to the equation—

$$C_6H_5CONHCH_2CO.NH.N_2OH + 2NH_3 =$$
$$= C_6H_5CONHCH_2CONH_2 + N_3.N_3.NH_4 + H_2O.$$
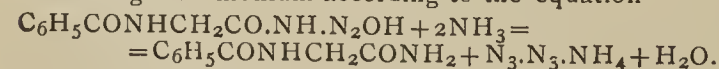
This diazohippuramide is obtained from hippuric ester in calculated quantity. A pound of the substance is covered in a two litre flask with 600 grms. of alcohol at 85 per cent, and whilst the flask is refrigerated ammoniacal gas is introduced to saturation. It is then allowed to stand for 24 hours, and the liquid is boiled with a reflux condenser until ammonia ceases to escape. After cooling for 12 hours the mass of crystals which has separated is drained and washed with cold alcohol. From the alcoholic filtrate 4 vols. ether precipitate about 70 per cent of the nitrogen ammonium in a pure state as a white powder. The rest of the compound can easily be recovered by re-crystallising the hippuramide from water, and mixing the mother-liquor with the ethereal alcoholic filtrates. It may thus be obtained as a lead, a silver, or a mercurous salt. The treatment of these compounds is very dangerous. The precipitated nitrogen-ammonium is washed with ether and dried in the air. The pure hippur-amide is re-converted into hippurylhydrazine with escape of ammonia by boiling with hydrazine-hydrate.

Diazohippuramide
$$(C_6H_5CONHCH_2CONH - N = N - OH).$$

The author will subsequently, in concert with H. Lang, describe this remarkable body in full. For the present I merely say that diazohippuramide is one of the substances most capable of reactions which I have ever encountered. It combines with the representatives of nearly all classes of bodies, organic and inorganic, partly in the cold and in two very different manners:—(1) either nitrohydrogen is split off (action of alkalies, ammonia, aniline, toluylendiamine, diamide, phenyldydrazine; (2) or there e-capes nitrogen (action of water, alcohol, halogenous alkyles, aldehyds, halogens, acidyl hydrazines).

(To be continued.)

THE BEHAVIOUR OF AZOIMIDE WITH LIVING ORGANISMS.*

By O. LOEW.

(Concluded from p. 288).

AN experiment executed on a rabbit by Dr. Pfeiffer, of the Hygienic Institute of Munich, in conjunction with the writer, gave the following results:—Eight minutes after the subcutaneous injection of 0·03 grm. sodium azoimide, there occurred muscular tremblings; ten minutes later increased secretion of saliva, lameness of the anterior extremities and retardation of the movements of the heart. After sixteen minutes, cramps, phenomena of lameness in the hinder extremities, inability to rise up again after falling. Soon afterwards, great difficulty of breathing, interrupted by single cramps, which continued until death —1 hour 44 minutes after the injection.

It may here be mentioned that I, after intentionally inhaling an atomised 1 per cent solution of sodium azoimide, soon experienced a ringing in the ears and headache, which lasted for about twenty-five minutes. Th. Curtius mentioned that free azoimide if respired occasions dizziness, headache, and inflammation of the nasal mucous membrane, and that the aqueous solution has a corrosive action upon the epidermis.

If we inquire the cause of the intense toxic action of azoimide, the most plausible view is the following :— Azoimide and its compounds are, as Curtius observed, easily decomposed and with a violent explosion. As the vital activity of the cells sets up decomposition by the transfer of violent atomic vibrations, the sudden decomposition of the azoimide compounds may react upon the protoplasm and occasion a re-arrangement of the active proteine matter.

In general, those cells and organisms will perish most rapidly by the action of azoimide, which decomposes it

most quickly. If the cells are ganglionic cells, such phe-nomena may act as irritations, and being conducted away in the nerves, they may appear as cramps in the muscles. The destructive process, introduced by rapidly succeeding irritations, can be propagated in the nerves like fire in a match, and bring the entire system into decomposition, when the death of the muscular and glandular system follows secondarily in consequence of the inaction of the heart and lungs.

In azoimide we have certainly another cause of toxic action from hydroxylamine and diamide. If the com-pound, supposed by Curtius, $NH_2 - NH - NH_2$, can be really isolated, we shall find it a most intense poison. In hydroxylamine and diamine we recognise a specific chemical action — an attack upon the aldehyd groups which occurs even if highly diluted. Azoimide will exert an action upon the aldehyds—if at all—only when in a very concentrated solution.

The slow action of sodium azoimide upon *Algæ* is very striking. We observe here that with a solution of 1 per 1000, granulations appear only after the lapse of several days, a fact which certainly indicates a slow decom-position, for if the sodium azoimide as such were capable of producing granulations, these would become visible in all spirogyrenous cells—at the furthest after some hours. Ammonia is probably formed, for whether in the free state or as carbonate, even at 0·1 per thousand, it produces the same phenomena of granulation. Ammonium salts of a neutral reaction act in the same manner at a concen-tration of 1 per 1000, but not at 0·1 per thousand. At the latter dilution ammonia exerts merely a nutritive influence.

Azoimide may apparently yield most readily ammonia by fission with water, nitrous oxide being formed simulta-neously, $N_3H + H_2O = N_2O + NH_3$.

As the chemical activity of protoplasm reminds us of catalytic actions, I tried if platinum black could produce a similar fission, and heated the small residue of 1 per cent solution of sodium azoimide, which I had at my disposal, with about 10 grms. of powerfully active platinum black. Immediately there occurred a violent disengage-ment of an indifferent gas, and the liquid, which had be-come highly alkaline, gave an extremely strong ammonia-cal reaction with Nessler's reagent. On the addition of dilute sulphuric acid the reaction became still more energetic. Azoimide, therefore, can in fact yield ammonia by catalytic decomposition, and thereby my view as to its action upon *Algæ* acquires more probability. As already mentioned, I consider its far more rapid action upon other organisms of a vegetable or animal origin from a different point of view.

DISSOCIATION OF PHOSPHONIUM BROMIDE.

By G. S. NEWTH.

IT is a well-known fact that phosphonium chloride is completely dissociated at ordinary temperatures into phosphoretted hydrogen and hydrochloric acid, and that the compound can only exist under the influence of either cold or pressure. The corresponding compound with hydrobromic acid, however, is much more stable, and if the two gases, phosphoretted hydrogen and hydrobromic acid, be mixed together, white fumes are at once pro-duced, which condense at the ordinary temperature to a solid mass resembling ammonium chloride in appearance. The compound, however, undergoes partial dissociation even at the ordinary temperature, which may be shown by the following simple device, which forms a very con-venient and striking lecture experiment for illustrating the phenomenon of dissociation. A glass tube 30 c.m. long and 10 m.m. bore, has blown upon it two small branch tubes at a short distance from the ends ; the stem of a long clay tobacco pipe is passed through the glass tube,

projecting about 2 c.m. beyond each end, and secured in its place by small pieces of caoutchouc tube being inserted between the glass and the clay pipe,—the whole resem-bling an ordinary Liebig's condenser in miniature, with a pipe-stem for the inner tube. As it is not often that a pipe-stem of the length required is found sufficiently straight to allow of its passing down a glass tube of the size mentioned, two short pieces may be joined together by a piece of caoutchouc tube. A slow stream of hydrogen is then passed through the glass tube, and burnt at a fish-

tail burner which is screwed into a short piece of lead pipe, and connected to one of the branch tubes of the apparatus, which may be conveniently supported in a horizontal position. A small U-tube, containing a few crystals of phosphonium bromide, is connected to one end of the clay pipe and a slow stream of hydrogen gas passed through. Almost immediately the flame of burning hydrogen will become coloured with the characteristic appearance due to the presence of phosphorus, the comparatively light phosphoretted hydrogen having dif-fused through the porous clay pipe into the stream o
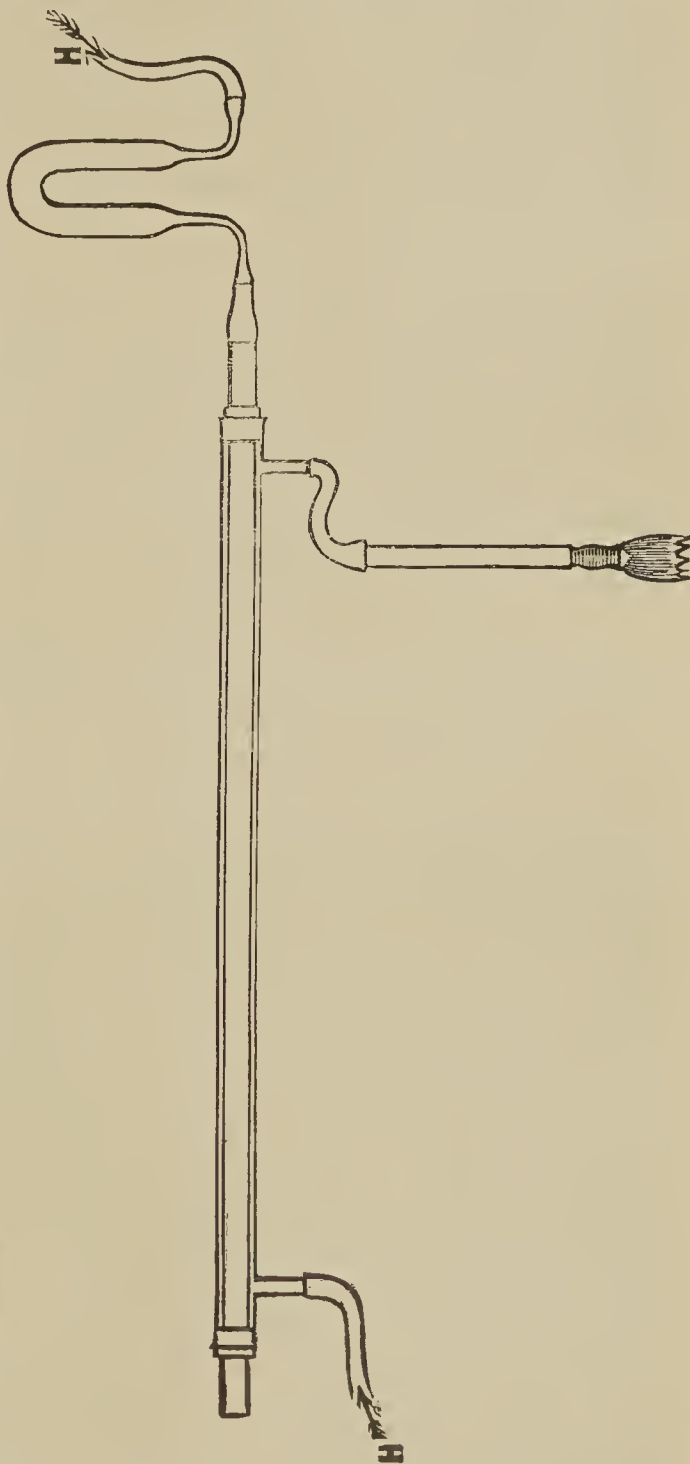
hydrogen circulating through the glass tube. A piece of blue litmus paper exposed to the gas which issues from the open end of the clay pipe will be at once reddened. If the U-tube be slightly warmed by merely grasping it in the hand, the effect will be still more marked.

The phosphonium bromide is readily obtained by delivering into a flask, immersed in a freezing mixture, a stream of phosphoretted hydrogen and of hydrobromic acid through separate tubes ; the two gases combine and the salt deposits upon the sides of the flask. The phosphoretted hydrogen may be prepared by the action of phosphorus upon alcoholic potash, and should be collected in a gas holder. The hydrobromic acid is most conveniently obtained by the method described in the CHEM. NEWS of October 30, as by that plan of preparing it the stream of gas can be regulated practically to any desired rate.

The phosphonium bromide obtained in the flask is for greater convenience transferred to a number of small U-tubes, the ends of which are drawn out. This is effected by removing the flask from the freezing mixture, and fitting into it a cork carrying two tubes, one of which passes nearly to the bottom of the flask. A stream of hydrogen is passed through the flask, which may be very gently warmed, and the issuing gas led through one of the U-tubes, which is placed in the freezing mixture. In a few minutes sufficient of the compound will have condensed in the tube, which may then be sealed off. In this way a number of tubes may be quickly filled.

NOTE ON AN

ELECTROLYTIC METHOD OF PREPARING METALLIC ALLOYS, &c.

By H. N. WARREN, Research Analyst.

THE following method of preparing metallic alloys, such as silicides, chromides, bronzes, &c., has lately been satisfactorily followed. It differs slightly from the manner in which mercury amalgamates, or alloys, with other elements, owing to its liquidity. By substituting for the mercury, iron, copper, zinc, &c., these metals may be readily made to combine with the more oxidisable elements, such as silicon, boron, phosphorus, &c., by so arranging the process that the metal forming the alloy, when in a fluid state, is connected to the negative pole of a voltaic series, and in direct contact with the substance containing the element with which it is desired to combine it. The apparatus employed consists of a deep conical crucible, through the bottom of which is inserted a pointed graphite rod, projecting about an inch within, the remaining portion being protected by passing through an iron tube coated with borax in order to prevent oxidation when exposing the same to an elevated temperature. The further extremity is next furnished with a binding screw or clamp, and connected negatively with the batteries employed, the whole arrangement being raised to a temperature sufficient to render liquid the metal introduced to form the alloy. Taking, for instance, the preparation of silicides, having introduced into the crucible a sufficiency of metallic copper, add sufficient potassium silico-fluoride to form when melted a layer about two inches in depth ; a thick platinum wire is now arranged so that its point just touches the surface of the melted silico-fluoride (care being taken that the melted copper remains sufficiently low so as not to come in contact with the positive pole or platinum wire, otherwise the action is, of course, neutralised and the power of the batteries uselessly exhausted).

To this wire is connected the positive pole of not less than two large cells of the ferric chloride battery, when an instantaneous action is at once perceptible ; dense white clouds of hydrofluoric acid are at once evolved from the platinum wire ; the potassium silico-fluoride

becomes in part decomposed, the whole of the silicon thus set free uniting with the metallic copper, to form a brittle silicide. Phosphor and other bronzes may, by slight alteration, be also readily formed.

The earthy metals, barium, strontium, and calcium, have as yet not been satisfactorily obtained as alloys.

Everton Research Laboratory,
   18, Albion Street, Everton, Liverpool.

ON META-TITANIC ACID AND THE ESTIMATION OF TITANIUM BY HYDROGEN PEROXIDE.*

By Prof. F. P. DUNNINGTON.

THE detection and estimation of small amounts of titanic acid, which has long been very tedious and unsatisfactory, has been rendered exceedingly simple through the publication of A. Weller in the *Ber. der Chem. Ges.*, 1882, of a method depending upon the production of a compound of intense yellow colour by the addition of hydrogen peroxide to the solution of titanium.

Since its publication I have made considerable use of this method, but have recently noted a feature in the test which must be kept in view to avoid error. The solution of the melt obtained by fusion with acid sodium sulphate when made with dilute sulphuric acid of five or more per cent, gives constant results, which tally with those made gravimetrically ; but when water only or very dilute acid is employed, one may obtain lower results. Upon one occasion a colouration was obtained which corresponded to only about one-third of the titanium which was afterwards found to be present. Moreover, if we take a slightly acid solution of titanium sulphate, dilute it and heat until it is partially precipitated, cool, re-dissolve with sulphuric acid and then add hydrogen peroxide, the yellow colouration will correspond to only a portion of the titanium present. I find an explanation of these facts in the formation of some meta-titanic acid. It is uniformly stated that when titanic acid is precipitated by heating a not too acid solution, it separates in the form of meta-titanic acid.

In order to further examine the meta-titanic acid which was in part described by Weber (*Jahr.*, 1863, p. 210), I have isolated it as follows :—Heat a dilute solution of titanium sulphate to 100° C. ; gradually add ammonia to excess, filter, treat the washed precipitate with hydrochloric acid, and warm ; there results a residue which is nearly insoluble in strong hydrochloric acid. Now wash this once or twice by decantation with cold water, and, when most of the hydrochloric acid is removed, there will be left a mass perfectly and readily soluble in cold water.

Again, if the above precipitate is treated with hydrochloric acid, and then evaporated upon the water-bath to remove the latter acid, there is left a mass of scales of a gummy appearance, which dissolves in a moderate amount of water, giving an opaline solution. This substance is practically free from chlorine and contains one molecule of water to one of titanic acid—and so presents the composition of the air dried meta-titanic acid of Merz. If either of these water solutions of meta-titanic acid be treated with hydrogen peroxide, it will not be coloured yellow, but afford a white precipitate.

It therefore appears probable that after the fusion of titanic oxide with acid sodium sulphate, if the melt is digested in water only, the solution of the free acid may occasion sufficient heat to form some meta-titanic acid, which when re-dissolved by the further admixture of acid would not be coloured by the hydrogen dioxide.

And we conclude that in making the estimation of titanium by the method of A. Weller, the "melt," after cooling, is to be digested in dilute sulphuric acid of such

strength as will prevent the formation of a precipitate even in warm solutions of titanic sulphate; for this purpose 5 per cent acid is found to answer.

ON THE OCCURRENCE OF NITROGEN IN URANINITE, AND ON THE COMPOSITION OF URANINITE IN GENERAL.*

By W. F. HILLEBRAND.

(Concluded from p. 293).

Special Experiments Relating to the Nitrogen in Uraninite.

THE last observation led naturally to a series of experiments as to the behaviour of the nitrogen on heating in air, in carbonic acid, and in hydrogen, in the hope that thereby some clue might be obtained as to its probable condition in the mineral. They were all made on the material which had served for the final and most careful analysis of Glastonbury uraninite (No. V.), not only because of the greater quantity at disposal, but also because of its high percentages in UO_2 and N. The results were in some respects perplexing to the last degree, and as yet no satisfactory explanation has been found. The mineral contained:—UO_2 59·93, UO_3 23·03, N 2·41, H_2O 0·43, Fe_2O_3 0·29, total U as UO_2 81·67.

Effect of Heating in Air.—After ascertaining that no nitrogen could be obtained either by sulphuric acid or sodium-potassium carbonate when the mineral had previously been heated for a sufficient length of time in air, the following experiment was made to show if the final change in weight represented the difference between loss of water plus all nitrogen and gain of oxygen from oxidation of UO_2. The weight of ignited material, after determining water, in nearly all uraninites, had indicated that this could not be the case.

1·0028 grm. dried at 100° C. :—

	Grm.
When heated below redness gained	0·0063
When heated at full redness for six hours gained	0·0020
,, ,, ,, ,,	0·0007
,, ,, ,, ,,	0·0000
	0·0090

Of the ignited product, 1·0060 grm., equivalent to 0·9970 grm. of unignited mineral, was decomposed in a sealed tube with dilute sulphuric acid. No nitrogen whatever was given off, and an amount of UO_2 was found representing 27·82 per cent of the unignited mineral. The UO_2 which had been oxidised to UO_3 therefore was 59·93 —27·82, or 32·11 per cent, which requires 1·90 per cent oxygen. The theoretical change in weight, assuming no nitrogen to have been expelled, would be the algebraic sum of the oxygen taken up, of the water driven off, and the small and uncertain additional loss which is shown by the gain of a calcium chloride tube when no sodium carbonate is used in the water determination, and which amounts to about 0·0012—0·0015 g. This would be 1·90 —(0·43+0·13), or 1·34. Assuming all nitrogen to have been expelled, there should appear a *loss* of 1·07, and such a result was to be expected in view of the failure to find nitrogen in the ignited matter. The actual result would indicate that only 0·44 per cent of nitrogen had been expelled by prolonged heating. If this is so no other explanation seems possible than that the nitrogen has entered into some other state of combination in which it is not set free by sulphuric acid or by fusion with an alkaline carbonate.

It is of the highest importance to ascertain definitely if the nitrogen is given off in whole or in part by heating in an oxidising atmosphere, but there are difficulties connected with the carrying out of such an experiment which have hitherto prevented its being made. It is intended,

however, to try the experiment of heating in oxygen and absorbing the latter by chromous chloride, after the manner recommended by Jannasch and Meyer (*Ann. d. Chem.*, 1886, vol. ccxxxiii., p. 375) for nitrogen determinations in organic bodies.

Effect of Heating in Carbonic Acid Gas.—I. 1·0722 grm. (dry) heated in carbonic acid generated from manganese carbonate lost 0·49 per cent in weight and afforded but a doubtful trace of nitrogen.

II. 1·0111 grm. (dry) when treated in a similar manner for a longer time lost 0·69 per cent in weight, and gave, approximately, 1·4 c.m.[3] of gas or 0·17 per cent by weight of nitrogen. After several hours further heating the boat had lost no more in weight, and no additional gas seemed to be given off. Because of the impossibility of freeing the carbonic acid from all traces of atmospheric nitrogen, —a copper roll having been used to retain its oxygen,—it is impossible to say with any certainty whether small fractions of a c.c. of gas were derived from the mineral or not.

Effect of Heating in Hydrogen.—The effect of heating in dry hydrogen was a reduction of practically all UO_3 to UO_2 and a slow expulsion of nitrogen; at least the usual methods showed less and less according to the duration of the heating. The following are the data obtained :—

I. 1·1287 grm. (dry), after being heated for three hours in a combustion tube in a current of hydrogen purified by potassium hydrate and sulphuric acid, had suffered a loss of 0·0198 grm. Of the ignited mineral 0·8022 grm. gave 1·62 per cent of nitrogen calculated to the original weight before reduction, and 0·3000 grm. required potassium permanganate equivalent to 81·18 per cent of UO_2 on the same basis. In view of the long heating required to reduce the percentage of nitrogen appreciably, it was not deemed practicable to collect any of it, because of the difficulty of getting rid of such a large quantity of hydrogen and the impossibility of freeing the latter entirely from atmospheric nitrogen. When transferred to a eudiometer and exploded with air and electrolytic oxyhydrogen, the gas was found to be absolutely free from hydrogen, which it was thought might have resulted from the action of reduced iron on the acid. An evolution of hydrogen was observed at first, and the tube was not filled with carbonic acid till this had entirely ceased. The fact that not quite the theoretical amount of UO_2 was found indicates that reduction was not complete. More than the theoretical amount should have been found, owing to the ferrous iron formed on solution in acid.

It was proved by passing the gases from the combustion tube through dilute hydrochloric acid and evaporating the latter with platinic chloride that no ammonia whatever was formed.

The loss in weight above given should represent the water in the mineral (0·0049), the oxygen of the UO_3 reduced to UO_2 (0·0148), all the oxygen of the iron existing as ferric oxide, possibly the oxygen of lead oxide, and lastly an amount of nitrogen represented by the difference between the original percentage (2·41) and 1·62, the residual percentage. The water and the oxygen of the UO_3, however, alone amount to 0·0197, or just the total loss.

II. 1·5700 grm. (dry) gave a loss of 0·0316 grm. after six hours heating in hydrogen. 1·1179 grm. of the reduced mineral gave 1·05 per cent of nitrogen, and 0·4177 grm. gave 81·46 per cent of UO_2, both calculated to unreduced mineral. The loss in weight should represent 0·0067 water, 0·0206 oxygen from UO_3, an uncertain amount from Fe_2O_3, and possibly from PbO, and the difference between 2·41 and 1·05 per cent nitrogen. But it does not exceed the sum of water and oxygen alone, and as in the first experiment no nitrogen seems to have been removed, although quantitative tests show that much has disappeared. Further tests at a higher temperature in a crucible, whereby some lead was reduced and partly volatilised, showed that all the nitrogen could be caused to disappear.

These results are as perplexing as those obtained by heating in air, and the explanation when found will doubtless lead to one for the other case. The apparent failure to expel nitrogen by hydrogen might be taken as additional evidence of its combination with uranous uranium, but it is as difficult to conceive why it should not still be set free by sulphuric acid after reduction of the UO_3, as after oxidation of a portion of the UO_2 to UO_3.

Conclusions.

Briefly summarised, the conclusions are as follows :—

1. Nitrogen exists in uraninite in quantities up to over 2·5 per cent, and seems generally to bear a relation to the amount of UO_2 present. This is the first discovery of nitrogen in the primitive crust of the earth, for the nitride of iron found by Silvestri (*Gaz. Chim. Ital.*, 1875, vol. v., p. 303) in lavas from Etna is of recent and secondary origin. It is rather strange that no works on mineralogy, so far as I am aware, make mention of his species.

2. The condition in which the nitrogen exists is unknown, but it is entirely different from any hitherto observed in the mineral kingdom, being liberated as nitrogen gas by non-oxidising acids and by fusion with an alkaline carbonate. Fusion with caustic alkalies does not give rise to the formation of ammonia, but probably liberates nitrogen.

3. Analysis of uraninite from various localities has shown that, with in general the same constituents, the mineral varies widely in composition, and that its physical characteristics and its behaviour toward certain solvents are often as distinct as the chemical differences.

4. The formulæ of Comstock and Blomstrand are in applicable to the zirconia, thoria, and yttria uraninites o North America and Norway, among which are to be reckoned bröggerite, cleveite, and nivenite, and probably to the varieties free from earths.

5. Extended and most careful examination of uraninite specimens from all possible localities is necessary before any conclusion worthy of acceptance can be reached as to the character of the chemical combination, or combinations, represented by them. The work in this direction should likewise cover a study of the nitrides and oxy-nitrides of uranium and thorium, with synthetical experiments aiming at the artificial production of uraninite.

This latter work will probably be undertaken in this laboratory as opportunity may offer, together with some further experiments on some of the material already examined. It is earnestly to be hoped those possessing or in a position to procure uraninite specimens will take the trouble to examine them on the lines suggested in this paper, or if unable to do so, will kindly contribute material for examination here.

The interest in the matter is not confined merely to a solution of the composition of this one mineral; it is broader than that; and the question arises: May not nitrogen be a constituent of other species in a form hitherto unsuspected and unrecognisable by our ordinary chemical manipulations? And, if so, other problems are suggested which it is not now in order to discuss.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.
December 3rd, 1891.

Prof. A. CRUM-BROWN, F.R.S., President, in the Chair.

MESSRS. T. M. Wyatt and Peter McEuan were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Frederick Edward Adams, Town Hall, Bolton; John Edward Whitley M. Fall, Bankfield Road, West Derby, Liverpool; John C. Hewlett, 40, Charlotte Street,

E.C.; Robert Ludwig Mond, 20, Avenue Road, Regent's Park, N.W.; William Shields Myers, New York; George P. Daniell Smith, 26, Colebrooke Row, Islington, N.

The following were elected Fellows of the Society :— Harold Alger; George Alfred Ashcroft; George James Allen; Edward Charles Cyril Baly; Thomas William Berry; Samuel Francis Burford; John Bairstow; J. Treeby Barratt; John Redman Bovell; John C. Chorley; William A. S. Calder; George Edward Cory; Thomas Darling; Charles E. Eastwick; Percy Elford; Lionel William Fulcher; George German, Jun.; Alfred Daniel Hall; John William Heath; Archibald Hall; John Holliday; John Walter Leather; Lionel Ludlow; Robert Lennox; Rudolf Laurentz Leffler; John Willis Marshall; Daniel McLaren, B.Sc.; Joseph Morris; William Naylor; William P. R. Newlands; Thomas Neilson; Laurence Priestley; Abhayacharan Sauyal, M.A.; Charles K. Scott; Thomas Stephenson; Walter Thorp; A. W. Winterton; John Henry Wilson; Thomas Armistead Ward; Henry White.

The following papers were read :—

68. "*Phosphorous Oxide. Part II.*" By T. E. THORPE F.R.S., and A. E. TUTTON.

In this paper the authors continue their description of the properties of phosphorous oxide, P_4O_6. In their first communication (*Trans.*, 1890, 553) it was stated that the oxide rapidly became red when exposed to light; they have since obtained phosphorous oxide in large, well-defined crystals, unaffected by light, by repeatedly exposing a quantity of the freshly distilled oxide to sunshine for several months at a time, and decanting the melted oxide from the red phosphorus produced. Large crystals of the oxide may also be obtained by spontaneous sublimation in a vacuum, which remain unaffected by light so long as they retain their crystalline form; but if they are melted by the warmth of the hand, and then allowed to cool to the wax like form, reddening occurs on exposure to light. Hence it appears not improbable that the permanency of the crystallised oxide is in some way connected with its crystalline character.

Bromine acts energetically on phosphorous oxide in a manner similar, in the end, to the action of chlorine. In a closed apparatus, however, an intermediate change occurs, crystals of phosphorus pentabromide subliming, and phosphoric anhydride being also formed—

$$5P_4O_6 + 20Br_2 = 8PBr_5 + 6P_2O_5.$$
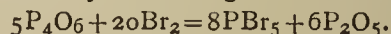
The pentabromide is afterwards washed down by the excess of bromine, and acts on the phosphoric anhydride, the ultimate result being that products are obtained corresponding to the equation $P_4O_6 + 4Br_2 = 2POBr_3 + 2PO_2Br$.

Iodine acts more slowly than bromine, forming crystals of P_2I_4. The interaction is best carried out in carbon bisulphide solution in a sealed tube at a temperature of 150° : $5P_4O_6 + 8I_2 = 4P_2I_4 + 6P_2O_5$.

Hydrogen chloride gas acts on phosphorous oxide, forming phosphorus trichloride and phosphorous acid : $P_4O_6 + 6HCl = 2PCl_3 + 3H_2PO_3$. A subsidiary change also occurs between the two products of the reaction, with formation of more or less phosphorus, orthophosphoric acid, and hydrogen chloride—

$$PCl_3 + 4H_3PO_3 = 3H_3PO_4 + P_2 + 3HCl.$$
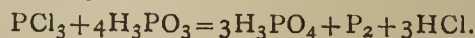
On distillation, a weight of phosphorus trichloride is obtained equal to that of the oxide employed.

When sulphur is heated with phosphorous oxide in a closed tube at about 160°, a most violent action takes place, the product of which is *phosphorus sulphoxide*, which is obtained in colourless, tetragonal crystals, upon sublimation in a vacuum. The crystals melt at about 102°, and the liquid boils constantly at 295° (corr.). Vapour density determinations show that the molecular formula of the sulphoxide is $P_4O_6S_4$.

It is a highly deliquescent substance, which rapidly dissolves in water, forming at first meta-, and subsequently ortho-phosphoric acid and hydrogen sulphide :

$P_4O_6S_4 + 6H_2O = 4HPO_3 + 4H_2S$. It is also soluble in carbon bisulphide, from which it is again obtained upon evaporation in tetragonal prisms.

Sulphur trioxide is reduced by phosphorous oxide, the sole products being sulphur dioxide and phosphoric anhydride.

Sulphuric acid dropped upon phosphorous oxide occasions great rise of temperature; with quantities of a grm. and upwards incandescence occurs. Sulphur dioxide is liberated, and phosphoric acid formed.

Sulphur chloride, S_2Cl_2, also acts with violence, forming phosphoryl and thiophosphoryl chlorides, sulphur and sulphur dioxide—

$$P_4O_6 + 6S_2Cl_2 = 2POCl_3 + 2PSCl_3 + 2SO_2 + 8S.$$
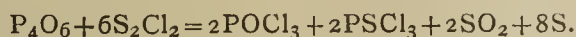
Ammonia gas acts slowly in the cold, but with incandescence on warming to $30°$. When ammonia is led over the oxide dissolved in ether, a white solid product is deposited, consisting of the diamide of phosphorous acid, $P(OH)(NH_2)_2$, and a small quantity of the corresponding ammonium salt—

$$P_4O_6 + 8NH_3 = 3P(OH)(NH_2)_2 + P(OH)_2(ONH_4)_2.$$

Phosphorous diamide is a white powder which is instantly dissolved by water with sufficient rise of temperature to induce incandescence. Treated with dilute hydrogen chloride solution, it evolves pure, non-spontaneously inflammable, phosphoretted hydrogen, formed by the decomposition at the high temperature of the reaction of the phosphorous acid first formed—

$$P(OH)(NH_2)_2 + 2HCl + 2H_2O = 2NH_4Cl + P(OH)_3.$$
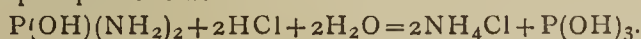
Nitrogen peroxide vapour oxidises phosphorous oxide in the cold to phosphoric anhydride, being reduced to nitrogen tri- or di-oxide.

Phosphorus pentachloride acts with great energy on phosphorous oxide. The action may be controlled by cooling with ice. A liquid mixture of phosphorus and phosphoryl trichlorides is produced—

$$P_4O_6 + 6PCl_5 = 6POCl_3 + 4PCl_3.$$
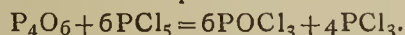
Phosphorus trichloride and phosphorous oxide only interact at a temperature near the boiling-point ($173°$) of the latter, and in a closed vessel; under these circumstances no phosphoryl trichloride is formed, but a solid mixture of pentachloride and pentoxide of phosphorus, together with amorphous phosphorus.

Hydrogen, phosphoretted hydrogen, carbon monoxide, carbon dioxide, sulphur dioxide, nitrogen, nitric oxide, cyanogen and ethylene, have apparently no action upon either cold or warm phosphorous oxide.

DISCUSSION.

Prof. RAMSAY inquired on what grounds the authors came to the conclusion that the amide described was a phosph*orous* and not a phosphoric compound, such as is represented by the formula $OPH(NH_2)_2$ corresponding to the formula $OPH(OH)_2$ for phosphorous acid, which latter he thought was undoubtedly a phosphoric compound. The low boiling-point and other properties of the sulphoxide described seemed to lend additional support to the view that phosphoric oxide was a compound of high molecular weight.

Dr. ARMSTRONG remarked that the conventional view that the affinity of phosphorus for oxygen was very great was somewhat disturbed by the observations now described, showing that in many cases the phosphorus and oxygen in phosphorous oxide were readily separated; it would seem that the extreme stability of phosphoric oxide was probably conditioned by peculiarity of structure.

The authors, in their reply, said that they had no special experimental proof of the constitution of the diamide formed by the action of ammonia; Prof. THORPE, however, expressed the opinion that the balance of evidence was in favour of the view that phosphorous acid *is* $P(OH)_3$.

69. "*Frangulin. Part II.*" By T. E. THORPE, F.R.S., and A. K. MILLER, Ph.D.

In the first communication to the Society by one of the authors, in conjunction with Mr. H. H. Robinson (*Trans.*, 1890, 38), it was concluded that frangulin had the composition $C_{22}H_{22}O_9$. This conclusion was based on analytical results alone, and it was, in fact, pointed out that the percentage yield of emodin obtained on hydrolysing frangulin agreed better with Schwabe's formula, $C_{21}H_{20}O_9$.

The authors have now prepared a larger quantity of frangulin, and have succeeded in obtaining it more nearly in a state of purity than was previously possible. They find, however, that crude frangulin contains a substance isomeric with emodin, which clings to it very persistently, and which it is very difficult to completely remove from the frangulin; they ascribe the conflicting statements of previous experimenters to the presence of this substance.

They have succeeded in proving the correctness of Schwabe's formula, $C_{21}H_{20}O_9$. Their conclusions are based not only on their more recent analyses of frangulin, but also, and in fact mainly, on the results obtained from the hydrolysis of frangulin. The two products of the hydrolysis are *emodin*, $C_{15}H_{10}O_5$, as shown in the first paper, and *rhamnose*, $C_6H_{12}O_5$. The latter substance was obtained in a crystalline form, and was identified by its chemical and physical properties and by the properties of its osazone. The percentage yield of emodin shows that one molecular proportion of frangulin yields one molecular proportion of emodin, and the difference represents one molecular proportion of rhamnose. It is thus possible to build up the formula of frangulin from its constituents, and since the result agrees with the formula deduced from the analyses of the glucoside, the conclusion is justified that frangulin has the composition $C_{21}H_{20}O_9$, and that its hydrolysis takes place in accordance with the equation: $C_{21}H_{20}O_9 + H_2O = C_{15}H_{10}O_5 + C_6H_{12}O_5$, which was given by Schwabe as highly probable.

The substance which has been mentioned as clinging so persistently to the frangulin has been isolated, and is found to have the same percentage composition as emodin. It melts at $202—203°$, and is, without doubt, the same substance which Schwabe found and described as melting at $199°$. It differs from emodin also in that it crystallises in golden-yellow needles, in the greater readiness with which it sublimes, and in its reaction with alkalis. It is probably an isomeric trihydroxymethylanthraquinone.

70. "*The Structure and Chemistry of Flames.*" By ARTHUR SMITHELLS, B.Sc., and HARRY INGLE, B.Sc., Yorkshire College, Leeds.

The authors have been engaged for twelve months in investigating the chemistry of flames produced by burning known hydrocarbons, and are still continuing their experiments. The publication of their results in the present form is consequent on the appearance of a paper by N. Teclu (*Journ. Prakt. Chemie*, xliv., 246), who describes the phenomenon which served as a starting-point in the authors' inquiry.

If a long glass tube be fitted by means of a cork over the metal tube of a Bunsen burner, so as to form a wider continuation of it, the flame can be caused to burn at the top of the glass tube. When the gas is turned slowly off the flame becomes smaller, and develops a sharply defined inner cone of a greenish colour; this cone ultimately becomes almost a flat disc of flame and enters the glass tube. It will, as a rule, descend at a rapid rate for some distance, then begin to oscillate and finally either detonate and light the gas at the bottom of the metal tube or else go out. If the gas supply be very carefully regulated, the flame may be got into such a state that it will descend the tube for a short distance and then re-ascend, and in this state it is very easy to see that whilst the lower cone is moving there remains at the top of the tube a steady cone of flame of a pale lilac colour. By heating the glass tube at one point, so as to *increase* at that point the rate of inflammation, it is possible to fix the oscillating inner cone—that is, to prevent its *re-ascent*. It is also possible

to effect this by narrowing the bore of the glass tube at one point, so as to *diminish* the rate of inflammation, *i.e.*, to prevent the *descent* of the inner cone past that point. In this way it is possible to separate the two hollow cones of combustion which constitute the Bunsen flame, and to keep them any distance apart for any length of time. This permits of the aspiration of the gases from the space between the cones without any chance of admixture of outside air or of products of combustion from the upper cone.

The apparatus used by the authors in most of their experiments consisted of two glass tubes, one of which slides very easily within the other. The inner tube (*c*), which is the longer one, is united to the outer one by an india-rubber collar (*a*), through which it slides freely, and the two tubes are kept coaxial by a ring of asbestos packing (*b*). The projecting end of the inner tube may be fitted to a Bunsen burner, but the authors have usually led separate supplies of gas and air into the apparatus by a T-tube, instead of using a Bunsen burner, in order to
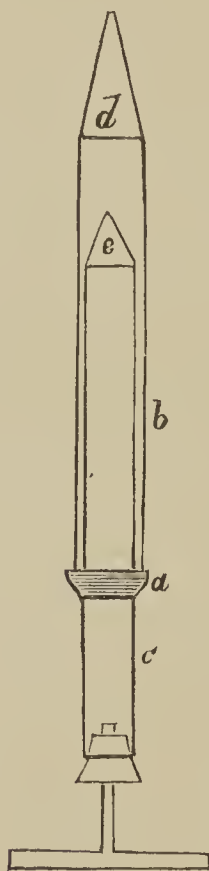
have a better control of the flame. With this apparatus a non-luminous flame is easily obtained, and the two cones can be separated in two ways. If the apparatus is arranged so that the flame is formed at the orifice of the wider tube (*d*), and the orifice of the narrower one (*e*) is 8 or 10 c.m. below it, on increasing the air supply the inner cone of flame will ultimately descend and rest upon the orifice of the inner tube. If, on the other hand, the inner tube be made to project beyond the outer one and the non-luminous flame be formed on it, then, if there be a sufficient air supply, on sliding up the outer tube it will, as it passes the flame, cleanly detach and carry up the outer cone, leaving the inner one still burning on the inner tube.

The authors have made similar experiments with flames of liquid hydrocarbons by charging air with the vapour of the liquid by passing it through a "saturator" such as is used for producing the ether-oxygen lime-light. The vapour charged air is afterwards mixed with more air, and by suitably regulating the proportions a non-luminous

flame is obtained and divided into two cones. In the case of liquid hydrocarbons, the lower cone of flame usually appears to be divided by dark spaces into several petal-like divisions which are in rapid rotation. In the case of benzene vapour the following sequence of appearances is presented:—Starting with the orifice of the inner tube, 8 or 10 c.m. below that of the outer one, a luminous smoky flame is first obtained at the latter; as air is gradually added the flame becomes less and less luminous, and an inner cone begins to develop, but before this has become non-luminous it descends to the inner tube; more air makes both it and the other cone non-luminous, and this state may be maintained. If now somewhat *less* air is supplied, a luminous streak appears at the tip of the inner cone, and passes right up and through the tip of the upper cone. If *more* air is supplied, the upper cone of the flame begins to disappear, and only the upper part of it remains; this also gradually fades away, and then there is only the lower cone left. Still more air produces a visible effect on the inner cone, the colour changing and the combustion becoming less intense until the cone rises from its seat, passes upwards and disappears. There is thus a gradual transition from the richly luminous flame to one consisting of a simple pale blue cone just on the point of extinction through excess of air.

The hydrocarbons examined by the authors were ethylene, methane, pentane, heptane, and benzene. Coal gas was also used. The gases from the regions between the two cones of flame were analysed in all these cases volumetrically or gravimetrically. The following are some of the results obtained:—

These results, which are obtained in the preliminary survey, are not quite accurate, owing to the impurity of the hydrocarbons and certain difficulties which are described in the paper. They show, however, that the products of combustion of the first cone are essentially CO_2, H_2O, CO, and H_2, and that the second zone is due to the combustion of the CO and H_2 with the external air.

The results are in harmony with the conclusions of Blochmann, obtained indirectly, and with the not generally known work of Dalton on the explosion of methane and ethylene with oxygen in quantities insufficient for complete combustion, which was repeated in 1861 by Kersten.

The authors point out (i.) that carbon, according to Baker's experiments, even in excess of oxygen, burns preferentially to CO, and not to CO_2; (ii.) that the heat of combustion of gaseous carbon to CO is probably greater than that of hydrogen to H_2O; (iii.) that, according to Dalton, CH_4 when burnt with its own volume of oxygen gives products represented in the equation—

$$CH_4 + O_2 = CO + H_2O + H_2;$$

and they conclude that this equation represents the character of the change first taking place in the inner cone. But as the two substances CO and H_2O act upon one another—
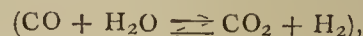
$$(CO + H_2O \rightleftharpoons CO_2 + H_2),$$

the case is one of reversible change, and four products will result, viz., CO_2, H_2O, CO, and H_2.

The conditions of equilibrium of this system, according to Dixon, are expressed by the coefficient—

$$\frac{CO \times H_2O}{CO_2 \times H_2} = 4\cdot0.$$

This is subject to certain conditions of temperature and dilution. The authors in their most reliable experiments (viz., the gravimetric ones), with ethylene and coal gas, get numbers not greatly differing from 4; but they are still engaged in studying this question.

The authors have succeeded in dividing into two cones flames produced by admixture of air with cyanogen, sulphuretted hydrogen, carbon bisulphide, and decomposed ammonia (*i.e.*, $N_2 + 3H_2$). The products of the inner cone in the case of cyanogen were found in one experi-

Substance.	C_2H_4.		CH_4.	C_5H_{12}.	C_7H_{16}.	C_6H_6.	Coal gas.		
	M.m.	M.m.	M.m.				M.m.	M.m.	M.m.
Diameter of outer tube	29	29	29	—	—	19	29	19·5	28
Diameter of inner tube	20	20	20	—	—	8	20	12	8
G (gravimetric) or V (volumetric) ..	G	V	V	V	V	V	G	V	V
CO_2	3·8	3·6	6·8	7·0	6·5	13·1	3·8	4·2	4·8
H_2O	9·5	9·5	17·6	13·1	12·3	7·7	14·9	16·0	15·9
CO	15·3	15 6	4·5	7·9	9·5	5·0	10·2	8·8	7·1
Hydrocarbons	0·8	1·3	—	—	—	0·6	—	—	—
H_2	9·5	9·4	3·9	5·4	5·8	0·64	10·9	9·3	7 7
N_2	61·1	60·6	67·2	66·2	65·6	73·1	60·3	62·0	64·4

ment to consist of CO and CO_2 in the proportion of 2 vols. of the former to one vol. of the latter.

Professor Smithells is continuing the experiments with a view of elucidating the following points:—

(i.) The influence of differences of diameter of the tubes and rates of efflux on the fractional combustion.

(ii.) The exact composition of the interconal gases in the case of hydrocarbons, and also of mixtures of $CO + H_2$, so as to ascertain if, and in what way, the coefficient—

$$\left(\frac{CO \times H_2O}{CO_2 \times H_2} = 4 \right)$$

varies with the composition of the gases and other conditions.

(iii.) The composition of the interconal gases from hydrocarbon flames whilst carbon is being liberated, so as to ascertain whether the luminosity of flame is due to simple decomposition of hydrocarbons by heat, to preferential combustion of hydrogen, to partial decomposition, or to other change.

(iv.) The exact nature of the flame of cyanogen, so as to ascertain what governs the proportions of CO and CO_2 formed in the inner cone.

(v.) The manner in which the partition of oxygen takes place in the inner cone between C and H, H and S, C and S, so as to obtain information as to the affinities of C, H, and S for oxygen.

(vi.) The spectroscopic appearances of the flames.

DISCUSSION.

Professor THORPE after expressing regret that time did not permit of the discussion of the numerous interesting questions which had been raised, referred to Professor Smithell's remark, that the books failed to notice the fact that carbonic oxide was produced on partial combustion of methane. He pointed out that Mr. Thomas, several years ago, made a special study of this question, having been led to do so by the observation that in cases of undoubted marsh gas explosions in coal mines the men killed often exhibited an appearance suggestive of carbonic oxide poisoning, Mr. Thomes found that carbonic oxide and hydrogen were regular products of the incomplete combustion of marsh gas. (*Cf.* "Coal Mine Gases and Ventilation," by J. W. Thomas. Longmans and Co., 1878. Also *Iron*, 1875).

(To be continued.)

PHYSICAL SOCIETY.
December 4th, 1891.

Prof. W. E. AYRTON, F.R.S., President, in the Chair.

MESSRS. P. L. Gray, A. Anderson, H. Davey, L. W. Fulcher, H. H. Hoffert, and W. Watson were elected members.

A paper on "*A Permanent Magnetic Field*" was read by Mr W. HIBBERT, A.I.E.E., F.I.C.

The author had noticed the approximate constancy of an "aged" bar magnet, and he obtained still greater constancy by attaching pole-pieces to a bar magnet, of such a shape as to give a nearly closed circuit of small "magnetic resistance." The pattern now described consists of a a steel rod 1 inch diameter and about 2½ inches long, with a cast-iron disc 4 inches diameter and $\frac{5}{8}$ thick, fixed at one end; the other end is fitted in a hemispherical iron shell which surrounds the bar and comes flush with the upper surface of the disc. An annular air space, less than $\frac{1}{16}$ wide, is left between the cylindrical surface of the disc and the inside of the shell; and when the bar is magnetised a strong magnetic field exists in this space. To use this field for producing electro-magnetic impulses, a coil of wire is wound, in a shallow groove, on a brass tube which can slide easily through the annular space, thus cutting all the lines. The tube is allowed to fall by its own weight, a neat trigger arrangement being provided for effecting its release.

The instrument exhibited had 90 turns of wire in the coil, and the total magnetic flux across the air space was about 30,000 C.G.S. lines. A large electro-magnetic impulse is therefore obtainable even through resistances as great as 10,000 ohms. Tests of three instruments show that there has been practically no magnetic decay in seven months. The author therefore considers them satisfactory, and is prepared to supply them as magnetic standards. To facilitate calculations the number of lines will be adjusted to a convenient number, say, 20,000 or 25,000.

Several uses to which the instruments are well suited are mentioned in the paper, and a simple way of determining permeability by the magnetometer method is described.

Mr. BLAKESLEY thought the name given to the instrument was inappropriate, for it really gave a constant impulsive E.M.F.

Dr. SUMPNER said the constancy of the sensibility of d'Arsonval galvanometers was a measure of the constancy of magnets having nearly closed circuits. Such instruments, in use at the Central Institution, had remained unchanged for several years.

Prof. S. P. THOMPSON admired Mr. Hibbert's instrument, and thought it would be very useful in laboratories. Standard cells, he said, were not always reliable, and condensers were the most unsatisfactory of electrical standards. On the subject of permanency of magnets, he said that Strouhal and Barus found that magnets with nearly closed circuits were most constant, and that, to give the best results, the hardness of the steel should be less the more closed the circuit. Mr. Hookham had also found that by using a nearly closed circuit and reducing the strong magnetisation by about 10 per cent, great constancy could be obtained.

Some years ago, he (Dr. Thompson) had tried the effect of ill-treatment on magnets, and observed that touching or hitting a magnet with non-magnetic material had little effect, whilst similar treatment with iron or magnets affected them considerably. Suddenly removing the keeper of a magnet tended to increase the magnetism, whilst putting a keeper on suddenly had the reverse effect. Strouhal and Barus had also investigated the temperature coefficient of magnets, and found that this might be reduced by subjecting the magnet to rapid changes of temperature after the first magnetism, and then re-magnetising.

Mr. W. Watson enquired what was the percentage fall in strength of Mr. Hibbert's magnets. The bars used in magnetic surveys had been tested frequently, and they lost about 0·5 per cent in six months.

The President asked what was the temperature co-effcients of the magnets described in the paper? Mr. Evershed, he said, thought it was between 0·01 per cent and 0·05 per cent for ordinary magnets. He thought the instrument shown by Mr. Hibbert would be of immense value if the magnet was really permanent. By it ballistic galvanometers could be readily calibrated, and, when combined with a resistance bore, it could also be used as a standard for current; for since the constant of a ballistic galvanometer for quantity can be determined from its constant for current, if the periodic time be known, conversely, that for current can be found from the constant for quantity. In some instances this would be of great use. Speaking of the temperature coefficient of condensers, he said that, in some cases, the specific inductive capacity of dielectrics diminished with rise of temperature, whilst in others it increased.

Mr. Hibbert, in reply, said he found the temperature coefficient of his magnets to be roughly about 0·03 per cent, but he had not investigated the matter very carefully. In making his measurements no correction had been made for the variation of capacity of his condenser with temperature.

Mr. Walter Baily, M.A., took the Chair, and

The President communicated "*A Note on Rotatory Currents.*"

The subject, he said, was probably familiar to most persons present, for it had been frequently referred to in the scientific papers. Alternate currents could be obtained from an ordinary direct current dynamo by making contact with two points in the armature, say by connecting these points to insulated rings on the shaft, and using extra brushes. A direct current motor, similarly treated, transforms direct currents into alternating currents or into mechanical power. If two pairs of points in the armature be selected, situated at opposite ends of two mutually perpendicular diameters, then two alternating currents, differing in phase by 90°, can be obtained; and by choosing suitable points in the armature, two, three, or more currents, differing in phase by any desired angles, can be produced. In ordinary motors, the connections for doing this would be troublesome, but the Ayrton and Perry form, which has a stationary armature, lends itself readily to this purpose, for contact can be made with any part of the armature with great facility. A motor of this kind was exhibited, in which contact was made with four equidistant points on the armature. On connecting opposite points through fine platinum wires, and running the motor slowly, the wires glowed alternately, one being bright whilst the other was dark, and *vice versâ*, thus demonstrating the existence of two currents in quadrature. When the four points on the armature were joined to the four corners of a square of platinum wire, the wires became incandescent in succession, the glow appearing to travel round the square, and suggesting the idea of rotatory currents. A Tesla alternating current motor was also driven by two currents differing in phase by 90° obtained from the armature of the Ayrton and Perry direct current motor above mentioned.

The ease with which currents differing in phase by any amount can be obtained from such a motor led the author to investigate theoretically the case of two circuits connecting opposite ends of two diameters inclined at any angle α. Calling the currents in these circuits at any instant, A_1 and A_2, he had found that—

$$A_1 = 2nE_0 \frac{\sqrt{(r_2 + \rho\frac{\pi}{2})^2 + \rho^2(\frac{\pi}{2} - \alpha)^2 - 2(r_2 + \rho\frac{\pi}{2})\rho(\frac{\pi}{2} - \alpha)\cos\alpha}}{(r_1 + \rho\frac{\pi}{2})(r_2 + \rho\frac{\pi}{2}) - \rho^2(\frac{\pi}{2} - \alpha)^2} \cdot \sin(pt + \phi),$$

where—

n = number of turns on armature per **radian**;
E_0 = maximum E.M.F. per convolution;
ρ = resistance of armature per radian;
p = angular velocity of rotation;
r_1 = resistance of external circuit in which current A_1 passes;
r_2 = resistance of external circuit in which current A_2 passes; and—

$$\tan\phi = \frac{\rho(\frac{\pi}{2} - \alpha)\sin\alpha}{r_2 + \rho\frac{\pi}{2} - \rho(\frac{\pi}{2} - \alpha)\cos\alpha}$$

A similar expression, in which r_1 is written for r_2, and r_2 for r_1, gives the value of A_2.

The phase angle between the currents is given by $\tan(\phi + \varphi)$

$$= \frac{(r_1 + \rho\frac{\pi}{2})(r_2 + \rho\frac{\pi}{2}) - \rho^2(\frac{\pi}{2} - \alpha)^2}{(r_1 + \rho\frac{\pi}{2})(r_2 + \rho\frac{\pi}{2}) + \rho^2(\frac{\pi}{2} - \alpha)^2 - \frac{(\rho\frac{\pi}{2} - \alpha)(r_1 + \rho\frac{\pi}{2})}{\cos\alpha}} \cdot \tan\alpha.$$

The expression for ϕ shows that the phase of the current in circuit A_1 is independent of the resistance r_1. On the other hand varying r_2 alters ϕ.

It was also pointed out that tan $(\phi + \varphi)$ is generally greater than tan α.

Prof. J. Perry, F.R.S., read a paper on "*Struts and Tie-rods Laterally Loaded.*" He pointed out that in the case of struts a slight want of straightness may considerably reduce the breaking load. Even if a strut be originally straight and the thrust properly distributed, its weight usually produces lateral loading and consequent bending. Similarly, centrifugal force produces lateral loading in connecting rods. For some years the author has given his students practical examples of struts and tie-rods to work out, taking into account the effect of lateral loads. The chief results obtained, together with a general treatment of the whole subject, are embodied in the paper. Where the curves of bending moment and the deflections due to lateral loading can be easily developed by Fourier's Series, solutions can readily be found. Simple cases of uniformly loaded struts and tie bars have been fully worked out, and also the case of locomotive coupling rods. In one problem on the latter subject a rectangular cross section was chosen and the proportions of depth to breadth determined so as to make the rod equally strong in the two directions when running at various given speeds. With cranks 12 inches long, the results show that at a speed of 390 revolutions per minute the ratio of depth to breadth must be infinite so as to give equal strength, so great is the influence of the lateral loading due to centrifugal force when combined with the thrust. Horizontal tie-rods loaded by their own weight have been investigated, and the tensions required to neutralise compression due to bending determined. A steel bar was used as a strut, with a thrust of 1500 lbs. The maximum stress due to bending by its own weight alone was 816, and on applying the thrust the maximum stress was raised to 23,190, or about twenty-six times that due to lateral loading alone. More complex cases have also been treated, the results of which are given in the paper.

OBITUARY.

PROFESSOR STAS.

The chemical world—indeed, we may say Science in general—has just experienced a severe blow by the death of Professor Stas, of Brussels. Although, perhaps, little known to the outside public, the deceased *savant* has earned undying honour and gratitude by his prolonged and splendid researches on the atomic weights of many of the elements. His laborious accuracy, his acuteness

in detecting possible sources of error, his fertility of resource in their elimination, and his conscientious determination to be satisfied with nothing less than unquestionable truth, will remain a model for all generations.   We purpose giving particulars next week.

NOTICES OF BOOKS.

An Introduction to Chemical Theory.   By ALEXANDER SCOTT, M.A., D.Sc.   London and Edinburgh : A. and C. Black.

OF elementary text-books, which are occupied almost exclusively by the enumeration of facts and the description of experiments, we have had of late years a plethora. But works which aim at bringing the results of observations and experiment into harmonious connection have been scarce indeed.   Now, when even zoology and botany have left behind them the mere descriptive stage, it is surely an opprobrium for chemistry to linger in the rear.

The author notices with due regret that "those who have had to teach the elements of both chemistry and physics to the same classes of students usually find the progress of their pupils more rapid and satisfactory, for a time, at least, in the latter subject."

This difference he ascribes, with great probability, to the smaller number of facts, apparently disconnected, which are required in physics before they can be grouped together and built up deductively." His undertaking, therefore, is most commendable, and we believe that it will contribute to a wider and clearer understanding of chemical theory.   Dr. Scott lays no claim, as regards the work before us, to either originality or completeness ; but matter which is scattered through the scientific journals and the transactions of the learned Societies requires to be collected and often explained before it can be available to the student.

In accordance with the destination of his book, the author confines himself within the boundaries of what may be regarded as fairly established, leaving speculative subjects for the study of another class of readers.

He arranges his subject-matter under the headings of The Constitution of Matter ; Atomic Weights ; Molecular Weights ; Classification of Elements ; Classification of Compounds, Acids, Bases, Salts, and Carbon Compounds ; Abnormal Vapour-densities and Dissociation ; Physical Properties of Compounds ; Thermo-chemistry ; Chemical Change ; Solution and Electrolysis.

Dr. Scott recognises that the laws of Boyle, Charles, and Avogadro are true only to a limited extent.   Prout's law is discussed at some length, mainly in order to throw light upon the determination of atomic weights. He considers that much may be said for this supposed law, if for the atomic weight of hydrogen we substitute $\frac{1}{16}$ part of the atomic weight of oxygen.

In considering the classification of the elements, he accepts the Newlands-Mendeleeff system, with certain reservations.

As regards formulæ and symbols, the author protests against their common use as a kind of shorthand to express *indefinite* quantities of the substances in question. This practice is very common in the abridged text-books now so abundant.   He insists that each term of an equation should refer to a definite number of molecules, and not of atoms as such.

Our ordinary notation, the author thinks, is sufficient for inorganic chemistry ; but for organic compounds the case is different.   Here, however, occur two questions :— Does not the chemistry of silicon closely approximate to that of carbon ? and, again, Can we suppose the atoms in each individual molecule arranged on a plane ?   Into this latter question the author enters to some extent when expounding the researches of Le Bel and Van 't Hoff.

In treating of solution, Dr. Scott decidedly leans to the "osmotic pressure" or "dissociation theory," and considers that the burden of proof should be laid upon the advocates of the "hydrate theory."

We can most strongly recommend this book to the notice of teachers as a guide for the studies of their more advanced pupils.   We are compelled to add—of teachers who are at liberty to follow their own judgment, unfettered by any "syllabus."

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences.   Vol. cxiii., No. 22, November 30, 1891.

On Boron Phosphides.—A. Besson.—The author mentions a curious reaction of boron phosphide. The product of its limited oxidation by means of dilute nitric acid, on evaporation to dryness, presents the aspect of nacreous laminæ, which, if dissolved in luke warm water, give with ammonia in excess a white gelatinous precipitate.   There appears to be formed under these conditions a peculiar phosphoboric acid, the ammoniacal salt of which is sparingly soluble.

Bromo-derivatives of Methyl Chloride.—A. Besson. —The monobromo-compound, CH_2BrCl, is a colourless liquid, which distils without decomposition at 68° with an odour resembling that of chloroform.   It does not solidify at —55°.   It becomes slowly coloured on exposure to air and light, with loss of bromine.   Its specific gravity at +15° is 1·90 ; its vapour density taken with Hoffmann's apparatus in watery vapour is 4·72 ; theory demands 4·50.   The corresponding bibromo compound, $CHBr_2Cl$, has been previously obtained by Jacobsen and Neumeister in the action of potassa on a chlorobromic aldehyd. These chemists ascribe to the compound a boiling-point between 123—125°.   This boiling-point must be lowered by several degrees so as to lie between 117—119°.   It solidifies at —32°, its vapour density (taken in the vapour of aniline) is 7·18, the theoretical value being 7·25.

A Modification of M. Berthelot's Calorimetric Bomb, and on the Industrial Determination of the Calorific Power of Combustibles.—Pierre Mahler.— This memoir does not admit of useful abstraction.

The Fixation of Free Nitrogen by Plants.—Th. Schloesing Fils and Em. Laurent.—The author's results are that there are inferior green plants which are able to obtain gaseous nitrogen from the atmosphere.   Under the conditions of their experiments bare soils, oats, mustard, cress, asparagus, have not fixed free nitrogen in measurable quantities.   It has been once more verified that under the same conditions peas are capable of fixing large quantities of atmospheric nitrogen.

Ammonia in the Atmosphere and in the Rains of a Tropical Region.—V. Marcano and A. Muntz.—The air in the tropical region studied (near Caracas, in Venezuela), is, contrary to expectation, less rich in gaseous ammonia than that of temperate climates.   There is an abundant formation of nitric acid in the air of tropical countries, so that the ammonia combining with this acid ceases to be gaseous and forms crystalline dust.

Influence of the Solar Rays upon the Ferments met with on the Surface of Grapes.—V. Martinand.— It is found that grapes growing on the lower shoots of the vines yield a very large quantity of *Saccharomyces*, among which *S. apiculatus* predominates. On grapes from the middle height and from the summit of the vines, the ferments are very few in number. *S. ellipsoideus*, which is the most useful yeast for the fermentation of wine, is the more plentiful the less intense are the solar rays.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. vi., Nos. 6 and 7.

A New Acetylenic Carbide, α-Naphthylacetylene.—A. J. Leroy.—This compound is a colourless liquid boiling at 143—144° under a pressure of 25 m.m. Its composition is shown by the formula $C_{10}H_7 - C = CH$. It precipitates Báhal's reagent (alcoholic silver nitrate).

Organic Molecular Combinations obtained by Fusion (Aromatic Hydrocarbons).—Leo Vignon.—If we have a mixture of two definite fusible solids, which do not react with each other chemically in the ordinary sense of the word, and if we determine their melting-point, we find that it generally differs from the mean of the melting-points of its two components. This has been observed in case of mixtures of metals, fusible salts, and fatty acids. The author, experimenting upon a great number of bodies of definite and varied functions, has observed the same phenomenon. From the totality of the facts it results that the systems examined as regards their fusibility may be distinguished into two groups : A, mixtures without anthracene ; and B, those containing anthracene. The author represents the characters of the two classes graphically. The melting-point of any given anthracenic system increases regularly with the proportion of anthracene, and is always a little higher than the calculated melting-point.

Action of Chlorine upon Certain Acetones of the Fatty Series.—Demetrius Vladesco.

On Certain Nitro-derivatives of Dimethylate Ortho-Anisidine.—E. Grimaux and E. Lefevre.—These two memoirs do not admit of useful abstraction.

Production of Cuprous Acetylure by the Action of Acetylene upon Copper in Presence of Ammonia.—M. Kuntzmann.—This note requires the accompanying cut.

MISCELLANEOUS.

Whitaker's Almanack.—We have received from the publishers a copy of " Whitaker's Almanack " for 1892. The most important alterations to be noted in the contents of this valuable work are to be found in the enlargement of its sections. Additional space has been allotted to educational matters, and a separate article dealing with educational progress and occurrences is given for the first time. Agricultural education also forms the subject of a separate article. An article on our present ocean mail supplies a convenient record of the rise, progress, and best achievements of the great lines of ocean steamers. Naval gunnery and a synopsis of the results of the census are also amongst the subjects separately treated. Every page and almost every line of the work has been corrected, and as nearly as possible brought up to the date of issue. In many instances the changes wrought during the brief interval of a single year are so numerous that scarcely a line of the section in which the subject is dealt with remains unaltered.

The New " Methylated Spirit."—Not the least of the difficulties encountered by British industrial chemists in competing with foreign rivals has been the lack of cheap alcohol. To meet this difficulty the sale of " methylated spirit " was permitted,—a mixture, as most of our readers know, of alcohol with impure wood-spirit. This liquid was in many cases further contaminated with shellac, an addition objectionable to all consumers save the varnish-makers. Still the methylated spirit when free from resinous matter was no small boon, and was preferred, *e.g.*, by photographers to pure ethylic alcohol. The powers that be, however, were afraid that the article was too good for use in the arts, and have therefore enacted that it must be polluted by a further addition of coal naphtha ! The alleged reason for this step in the wrong direction is that

the methylated spirit was drunk by workmen and others to the injury of the revenue and the promotion of intemperance. The new preparation fills photographers and many chemical manufacturers with dismay. If such spirit comes in contact with water or any aqueous liquid it is at once rendered turbid and unfit for use. The hope that it will not be drunk is fallacious. We have known of hands at chemical works — seasoned topers — who would even toss off a " tot " or *petit verre* of the coal naphtha itself ! If the heads of the Revenue really wished to make the spirit undrinkable they should have prescribed the addition of Dippel's animal oil. A mere trace of this liquid, without interfering with the legitimate uses of the spirit, renders it so loathsome to smell and taste that no one would dream of drinking it. This is no untried expedient ; it is one of the legalised additions used in Germany for " denaturising " alcohol.

MEETINGS FOR THE WEEK.

TUESDAY, 21nd.—Photographic, 8.
WEDNESDAY, 23rd.—Geological, 8.

TO CORRESPONDENTS.

G.—A book by the Editor on the " Manufacture of Beet-root Sugar in England " was published some years ago by Messrs. Longmans.

THE CHEMICAL NEWS.

Vol. LXIV., No. 1674.

THE DENSITIES OF SULPHURIC ACID SOLUTIONS.

By SPENCER U. PICKERING, F.R.S.

A SHORT time ago Mr. H. D. Richmond (*Jour. Soc. Chem. Ind.*, 1890, p. 479), made use of my determinations of the densities of sulphuric acid solutions (*Chem. Soc. Trans.*, 1890, pp. 139—158), to construct a very full table of the values for strong solutions at 15° C. Not long afterwards Prof. Lunge (*Jour. Soc. Chem. Ind.*, 1890, p. 1017), feeling hurt, apparently, that anyone else's determinations should have been preferred to his own, published a paper—to which my attention has only recently been directed—in which he sought to cast obloquy on the accuracy of my values ; but as the method which he selected for doing so consisted in making misrepresentations so gross that no one who read my work would have paid the least heed to them, I should not have thought it worth while to say anything about it were it not that Mr. Richmond's labour runs the risk of being neglected by those for whose benefit it was intended, but who might not be inclined to examine the dry data from which he obtained his material.

Mr. Richmond says :—"The recent work of Pickering has placed at our diposal a series of determinations which is, without doubt, the most complete yet published, and from them I have calculated a table, giving for each 0·0001 of specific gravity the corresponding percentages of sulphuric acid. My reasons for preferring the determinations of Pickering to all other observers, are the precautions taken to observe accuracy, and the large number of determinations made, he having made nearly as many determinations as all the other observers put together." Mr. Richmond's table gave the values for 15° ; but instead of taking these from my table, which contained values for this same temperature as deduced from observations made at 8°, 18°, 28°, and 38°, he deduced them afresh from the observations at these latter temperatures, and it is satisfactory to find that he obtained practically the same values as I did ; he says :—"my figures on comparison agreed almost absolutely with those in his (Pickering's) table, in no case was there a difference of more than 0·00002 in the density ; the accuracy of the table, then, is beyond doubt."

In order to cast doubt on this accuracy Prof. Lunge boldly states that I maintain that the percentage strength of my acid was known to an impossible degree of nicety —ten times greater than that to which I said it was known—and, moreover, that I pretend to have obtained this accuracy by analysis, whereas I was most careful to point out that I did not rely on analysis, and that no analysis would have given me even such accuracy as that which I did obtain.

Prof. Lunge says :—" The enormous amount of his (Pickering's) observations, and the seemingly stupendous accuracy of those, indicating *thousandth's** of a per cent of H_2SO_4 in the acid, may possibly make them appear more trustworthy than ours to those who have not worked in the same field. But I cannot for one moment acknowledge this conclusion. Hundreds of tests made by myself with the greatest possible care and calibrated vessels and corrected weights, with constant checkings and re-checkings, have proved to me that estimations of strong sulphuric acid are already *very* good if they do not differ from one another by more than one unit in the first

decimal per cent, and that the utmost accuracy attainable, but most certainly not attained by the majority of workers, is ±0·05 per cent. If Prof. Pickering maintains (*Chem. Soc. Trans.*, 1890, p. 73) that his percentages are accurate to ±0·001, this *impossible* assumption is to my mind from the outset a reason for distrusting the accuracy of his figures altogether, and I believe that this impression will be conveyed to others as well who take the trouble of looking at the very tottering foundations of that seemingly stupendous accuracy. . . . All his hundreds of observations are founded upon the analysis of a sample of pure sulphuric acid. . . . The fundamental analyses were not made by Prof. Pickering himself, but by Mr. Crompton. . . . *Now these estimations of Mr. Crompton's vary between* 99·704 *and* 99·962 *per cent, that is, to the amount of* 0·26 *per cent,* and yet Prof. Pickering does not hesitate to assert that the percentages of his acids . . . are accurately known to the third decimal per cent." In his recently published book (" Sulphuric Acid and Alkali "), Prof. Lunge reiterates these views, and refers to the passage here quoted ; and again, when speaking of my freezing-point determinations (p. 134) he makes a similar remark, saying :—" But we must remark that the apparent extreme accuracy of the estimations is quite illusory, since, even with the best methods known and the greatest skill, a *reliable* estimation of the strength of sulphuric acid can only be made up to the *first* decimal of the percentage amount, the second decimal being uncertain by ±5, whilst in that memoir *four* decimal places are given ! The third decimal of the thermometric estimations must be equally uncertain."

Some of these objections have already been raised by Mr. Sydney Lupton, and it is tedious work to have to correct for a second time the blunders made by critics who decline to read the papers which they attempt to criticise. In the present case, indeed, it requires some self-restraint on my part not to accuse the critic of a wilful misrepresentation of statements, and a perversion of the facts of the case ; nowhere, either on p. 73 (*Chem. Soc. Trans.*) or elsewhere, have I maintained that the percentages quoted were accurate " to 0·001," nowhere have I asserted, either with or without hesitation, that they were known " to the third decimal per cent." On the contrary, ±0·01 per cent is the figure printed most clearly on p. 73, previously also on p. 72, and subsequently on p. 85, in the form of 1-10,000th. On pp. 72 and 73 there are eighteen lines, and, again, on p. 338 thirteen lines, devoted to inform readers that the results of Mr. Crompton's analyses were *not* taken for determining the strength of the acid, but that a method " more reliable than any analysis " was found and accepted, this method being based on the fact that the pure acid must have a higher freezing-point than an acid with excess of either water or anhydride, and the superior accuracy obtained by employing such a method is mentioned again on p. 84 as being the first of the three special advantages which my determinations offered for constructing a table of densities ; there is also a further allusion on the same page to the fact that this method, and not the analytical one was used, and I re-stated this fact in my answer to Mr. Lupton (*Phil. Mag.*, 32, p. 95).* What excuse, then, can Prof. Lunge have for the assertions which he has made ? His misrepresentations are so glaring and so confidently repeated that it seems scarcely possible to attribute them to mere carelessness on his part. Even the *relative* accuracy of the strength of the solutions— the only accuracy which was of importance for the immediate purposes of my work, as I have so often pointed out (*vide Chem. Soc. Trans.*, pp. 73, 85 ; *Phil. Mag.*, 32, p. 85)—does not correspond with his 0·001 per cent, for it

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* All italics are Prof. Lunge's.

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* For the purposes of differentiation the percentages taken were not corrected in accordance with the results given subsequently by the freezing-point method, because the correction would have had no appreciable effect whatever on the differential values. But this has nothing to do with Prof. Lunge's remarks, for he is speaking of the density table, for the construction of which the corrected values were taken.

was "one unit in the fourth decimal place of the percentage."

I may mention that I never impugned the accuracy of, or even alluded to, Prof. Lunge's determinations, though I believe that the three advantages possessed by my determinations for the construction of a table is not possessed by either his or those of any other experimentalist. Prof. Lunge does not seem to have understood these advantages, but by laying such stress on the fact that no analysis will suffice to determine the strength within ±0·05 per cent, he unconsciously brings forward a strong argument in favour of the accuracy of my results, which were based on a non-analytical method capable of five times this amount of precision. The other advantages for the construction of a table afforded by my determination were that they were very numerous, and were made with solutions of very nearly round percentage values. Their great number also, by affording data for the accurate determinations of the rate of change, diminished the chances of errors in the process of interpolation necessary in constructing a table.

It seems ridiculous to have to point out a second time (see *Phil. Mag.*, 32, pp. 94, 103), that the quotation of a value to a given decimal place does not mean that it is known with certainty, either as to its actual or relative magnitude, to that decimal place, and it seems still more ridiculous to have to call the attention of critics again to the fact that the probable error of the mean of a number of analyses is not the same as the extreme difference between any selected two of the individual results.

Prof. Lunge makes some other remarks which bear on my work, and they all show as much carelessness as those already discussed.

On page 114 there is a statement which is calculated to imply the existence of a great discrepancy between Thomsen's and my own heat determinations:—" The heat of neutralisation of 1 molecule H_2SO_4 by 2 molecules NaOH, in the presence of 400 molecules of water, is given by Thomsen =31,380 cals. Pickering (*Journ. Chem. Soc.*, 1889, p. 323) states it only 28,197 cals." As a matter of fact I never determined the heat of neutralisation of the acid, and never made any statement as to its value in the presence of 400 H_2O being different from that given by Thomsen; on the contrary, I showed that if we accepted Thomsen's value, and from it and my own results of the heat of dilution of the acid (Thomsen's were not extended far enough for this purpose), deduced its probable value for infinite dilution, we got 28,197 cals. —a result which is of considerable importance, inasmuch as this value agrees within experimental error with the normal values obtained in the cases of most other acids.

On page 126 Prof. Lunge mentions my having isolated the tetrahydrate of sulphuric acid (f. p. −25°), which contains 57·66 per cent H_2SO_4, and says that "by adding a little water or sulphuric acid its freezing-point is at once lowered to −70°," a statement which would make anyone sceptical as to the correctness of my observation. The fact is that a *gradual* lowering of the freezing-point occurs by the addition of acid or water, and only attains −70° when the total percentage of acid present is reduced to about 39 or raised to 71.

Lastly, on page 126 he says "a third hydrate, $SO_4H_2,2H_2O$, is assumed, because on diluting strong vitriol with water down to this point the largest contraction, viz., from 100—92·14 vols. take place." It has, however, been known for some time that the position of maximum contraction varies with the temperature, and a reference to pp. 84 or 148 of my paper would have shown Prof. Lunge that at 18° it does not occur at 73 per cent, the composition of the dihydrate, but at 68 per cent.

Prof. Lunge's reference to the contraction occurring on mixing sulphuric acid with water led me to calculate from his own results (Lunge and Isler, *Zeit. Angew. Chemie*, 1890, p. 131) the values for these contractions for different strengths of acid, and the values obtained led me to a somewhat unexpected conclusion, namely,

that the accuracy of his determinations "is by no means very great. On differentiating the values we get a series of numbers, $\dfrac{dC}{dp}$, which exhibit irregularities sufficiently large to be apparent on a superficial inspection, and which compare very unfavourably with those deduced from my own determinations (*Chem. Soc. Trans.*, p. 148), of which I have here given a few for the purpose of

Contraction in c.c. on the Formation of 1 grm. of Sulphuric Acid Solutions.

LUNGE.			PICKERING.		
P.c. Acid. *p.*	Contr. C.	$\dfrac{dC}{dp}$	*p.*	C.	$\dfrac{dC}{dp}$
100	0		91·025	0·03723	
		−0·00472			−0·00298
95·88	0·01946		90·046	0·04014	
		−0·00359			−0·00275
90·85	0·03760		89·031	0·04293	
		−0·00306			−0·00255
88·30	0·04541		87·958	0·04566	
		−0·00197			−0·00232
83·38	0·05508		87·036	0·04779	
		−0·00071			−0·00220
73·60	0·06201		85·958	0·05016	
		−0·00009			−0·00167*
69·70	0·06235		84·979	0·05180	
		−0·00023			−0·00158*
66·65	0·06304		83·566	0·05403	
		+0·00045			−0·00139
63·14	0·06145		82·982	0·05484	
		0			−0·00119
59·03	0·06147		81·985	0·05602	
		+0·00043			−0·00104
55·15	0·05982		81·093	0·05695	
		+0·00028			−0·00086
51·38	0·05776		79·985	0·05791	
		+0·00007			−0·00072
46·94	0·05744		78·990	0·05862	
		+0·00078			−0·00066
42·67	0·05410		78·254	0·05911	
		+0·00047			−0·00054
38·57	0·05216		75·957	0·06034	
		+0·00057			−0·00029
35·15	0·05021		74·004	0·06091	
		+0·00115			−0·00022
31·15	0·04562		72·023	0·06135	
		+0·00099			−0·00012
27·42	0·04194		70·098	0·06158	
		+0·00076			−0·00004
23·61	0·03906		68·101	0·06165	
		+0·00133			+0·00005
20·08	0·03435		66·133	0·06156	
		+0·00166			+0·00009
15·60	0·02792		64·891	0·06145	
		+0·00152			+0·00014
11·76	0·02211		64·112	0·06135	
		+0·00175			+0·00019
6·18	0·01234		62·041	0·06095	
		+0·00185			+0·00028
3·31	0·00703		59·989	0·06037	
		+0·00193			+0·00025
1·85	0·00422		57·889	0·05984	
		+0·00222			+0·00031
0·91	0·00213		55·877	0·05921	
		+0·00234			+0·00036
0	0		53·896	0·05849	

* These values are wrongly quoted in the Table at p. 148 of the *Chem. Soc. Trans.*, 1890, a miscalculation of the volume of one solution having been made. This should be 0·562069, instead of 0·562169 as there given; the density from which this value is deduced is given correctly on p. 139.

comparison. The magnitude of the errors in Prof. Lunge's values for $\dfrac{d\,C}{d\,p}$ must, I think, be taken as indicating the existence of errors of no less than 0·0005 or 0·001 in his values for the contractions; an error of 0·001 in the contractions represents from 0·001 to 0·0035 in his density determinations, or 0·23 in the relative percentage strengths of his acids, and must negative any claims to real accuracy which his determinations might have been supposed to possess.

THE SUPPOSED COPPER NITRIDE.

By P. L. ASLANOGLOU.

IN the *Phil. Mag.*, 3., xix., 100, July—December, 1841, W. R. Grove, M.A., F.R.S., refers to some of his electrolytical experiments, that when a piece of metallic copper is connected with the positive pole of a battery in a solution of ammonium chloride, and the negative pole of the battery is connected with a platinum plate which also dips into the solution, after a time the liquid becomes blue, and a chocolate coloured nitride appears to be formed of specific gravity 5·9, and 5 grains of the substance give off 0·107 inch of nitrogen gas when heated, leaving copper.

T. E. Thorpe,[*] Ph.D., F.R.S., and H. Watts,[†] B.A., F.R.S., F.C.S., refer to the above.

I have repeated the above experiment several times, and found the specific gravity of the substance to be 5·6. I have tested for nitrogen by Dumas's method, and obtained a negative result, therefore I suggested analysing the substance as an oxide of copper, and out of several experiments I have chosen the three following :—

Found percentages in grms.—

		I.	II.	III.
Oxygen	.. ..	7·8262	7·7954	7·6551
Copper	.. ..	91·8202	90·5482	88·6781
		99·6464	98·3436	96·3332

and taking the mean of the three experiments—

Oxygen	.. ..	7·7589
Copper	.. ..	90·3488
		98·1077

which approximately correspond to the formula of Cu_3O, being—

Oxygen	.. ..	7·8048
Copper	.. ..	92·1951
		99·9999

		Theory.	Found.	Difference.
Oxygen	.. ..	7·8048	7·7589	0·0459
Copper	.. ..	92·1951	90·3488	1·8463
		99·9999	98·1077	1·8922

With my experiments the copper found comes lower than that of the theory, the cause being that when heating the substance in a boat, testing for oxygen, some of the heated substance adheres to the sides of the tube, consequence of low percentages for copper.

Although by looking into the substance itself you cannot detect any metallic copper, yet on applying the elutriation system you can plainly see at the bottom of the agate mortar traces of metallic copper. Therefore the substance was covered with a saturated solution of

[*] "Inorganic Chemistry," vol. ii., "The Metals," p. 181, Section 139.
[†] "Dictionary," vol. ii., Con—Gyt, p. 67.

silver nitrate for the purpose of separating the oxide of copper from the metallic copper, and thus estimating the right formula of the substance :—

$$Cu_2O + Cu + 2AgNO_3 = Cu(NO_3)_2 + 2Ag + Cu_2O.$$
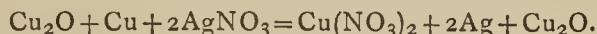
We let it stand in the cold for twelve hours and filter.

The residue $2Ag + Cu_2O$ is dissolved with HNO_3, and we precipitate the silver by HCl, and filter. The residue is AgCl, and the filtrate $Cu(NO_3)_2 + HNO_3$.

The AgCl is washed, dried, weighed, and determined as with the chlorides.
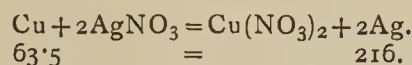
$$Cu + 2AgNO_3 = Cu(NO_3)_2 + 2Ag.$$
$$63·5 \qquad = \qquad 216.$$

$$AgCl \quad Ag \quad AgCl$$
$$143·5 : 108 :: 1·587 : x.$$

$$x = \frac{1·587 \times 108}{143·5}.$$

$x =$ amount of silver.

$$Ag \qquad Cu$$
$$216 = 63·5.$$

$$\therefore 216 : 63·5 :: x : z.$$

$z = \dfrac{x \times 63·5}{216} =$ amount of metallic copper contained in the original substance.

Found metallic copper—

I. 29·398
II. 29·142

The filtrate $Cu(NO_3)_2 + HNO_3$ is evaporated down and taken up with water, precipitating by NaOH the copper present, and determining it as oxide. This filtrate is to determine the copper oxide contained in the original substance.

Found copper oxide—

I. 69·9949
II. 71·6314

∴. Formula of the substance.

Found.

Oxygen	. .. .	7·759
Copper	. .. .	90·348
Metallic copper	.. ..	29·27
		61·078

Atomic Ratio.

Oxygen	.. .. ..	7·759 }	O.
Copper	.. .. ..	61·078 } = Cu₂ =	$Cu_2O + Cu$.
Metallic copper	..	29·27 }	Cu.
		98·107	

∴. Found formula of substance $Cu_2O + Cu$.

W. R. Grove, in the same volume of the *Phil. Mag.*, p. 102, says :—

"It may be worth remarking that the quantities of nitrogen which enter into combination with the metals in these experiments are in proportion to their affinity for oxygen, and it may perhaps be considered an argument in addition to the many already advanced to prove that nitrogen is an oxide."

On Epidibromhydrine. — R. Lespieu. — Symmetric dibromhydrine was treated with phosphoric anhydride and distilled under a reduced pressure, when the product obtained separated into two principal parts, tribromhydrine, boiling at 219°, and $C_3H_4Br_2$, passing over at 91° and decomposing at 155°.—*Bull. Soc. Chim. de Paris*, vi. No. 6.

NITROHYDRIC ACID.*

By TH. CURTIUS.

(Concluded from p. 300).

IF nitro-hydrogen is eliminated an affinity is set free on the hippuryl, and is satisfied by the radicle of the attacking body, e.g.,—

$$(Hipp)\ NHN_2.OH + 2NH_2C_6H_5 = (Hipp)\ NHC_6H_5 +$$

Aniline.   Hippurylanilide.

$$+\ NH_3H_2C_6H_5\ +\ H_2O\ ;\ or,$$

Nitrohydric Aniline.

$$(Hipp)\ NHN_2OH\ +\ 2N_2H_4\ =\ (Hipp)\ NHNH_2\ +$$

Diamide.   Hippurylhydrazine.

$$+\ NH_3H.N_2H_4.N_2H_4\ +\ H_2O.$$

Nitro-diammonium.
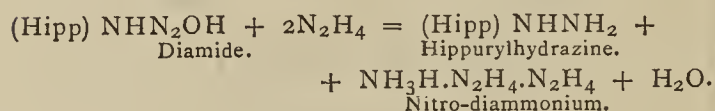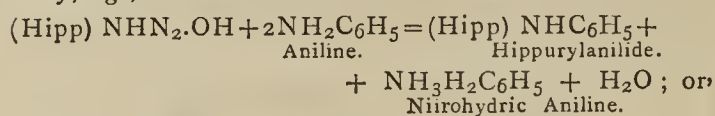
A mol. of water is always split off at the same time.

If, on the other hand, nitrogen is eliminated in the reaction, there are formed bodies which are derived from hippuramide by the substitution of an atom of hydrogen of the amido group, e.g.,—

$$(Hipp)\ NHN_2OH\ +\ C_2H_5OH\ =\ N_2\ +$$
$$+\ (Hipp)\ -\ NHOC_2H_5\ +\ H_2O\ ;\ or,$$

$$(Hipp) - NHN_2OH + C_6H_5CONHNH_2 = N_2 +$$
$$+ (Hipp)\ NHNHNHCOC_6H_5 + H_2O.$$
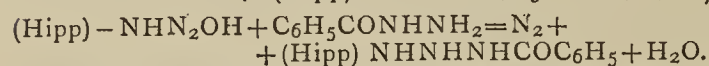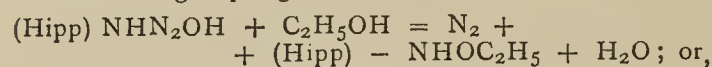
It will be seen that here also a mol. of water is split off.

Peculiar interest attaches to those derivatives which in the direction of the equation last given are formed by the action of primary acidylhydrazines upon diazohippuramide. These bodies must be regarded as symmetric bis-acidyl-derivatives of $NH_2.NH.NH_2$, a triamide not yet known in the free state. The analysis, the origin, and the behaviour of these substances leaves no room for doubt that there exists in these bodies an open unramified chain of three imido-groups which are united with radicles on each hand. These substances possess so great a stability against alkalies or mineral acids that it has not been hitherto practicable to split off the acid radicles and to set the nitro-hydrogen, N_3H_5, at liberty. It is scarcely to be doubted that further experiments will lead to the object and will be described in future.

Salts of Nitrohydric Acid. Nitrogen-Silver, N_3Ag.

Notwithstanding the remarkably explosive properties of this body (the silver in which has been already determined), an estimation of the nitrogen has been effected by combustion in a long column of copper oxide.

0·1076 grm. of this substance, when burnt with copper oxide, gave 26·0 c.c. of nitrogen at 6° and a pressure of 738·5 m.m., corresponding to 0·03077 grm. nitrogen at 0° and 760 m.m.

	Calculated for N_3Ag.	Found.
N/14	28·00	27·65 per cent.

The experiment succeeded once only; on repetitions, the tube, in spite of the most careful distribution of the material, was each time shattered.

Nitrogen-silver dissolves in ammonia, and crystallises on the evaporation of the ammoniacal liquid in needles, about a centimetre in length, nearly colourless, and fearfully explosive. The crystals explode sometimes on breaking. This compound is probably the silver salt and not a double ammonium compound, since the needles described are quite insoluble in water, and separate out only after the smell of ammonia has disappeared.

Nitrogen Mercurous Oxide. Nitrogen Calomel, N_3Hg.

This body is quite insoluble in water, like the silver salt.

If we wish to obtain nitro-hydrogen from the mother-liquors, they are best precipitated with mercurous nitrate,

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aspirated dry, and thoroughly washed out with water. This salt has the advantage over the silver salt that it is more permanent, requires a higher temperature for ignition than the lead compound, the latter of which is, moreover, soluble in an excess of the precipitant. The precipitated mercurous salt form micro-crystalline anisotropic needles, which take a yellow colour on exposure to light, without undergoing any further change.

0·3866 grm. of the substance yielded, with lead chromate, 55·4 c.c. of nitrogen at 11·5° and 758·5 m.m. pressure, corresponding to 0·0669 grm. nitrogen at 0° and 760 m.m.

0·3057 grm. of the substance on suspension in water and treatment with H_2S, gave 0·2936 grm. mercury sulphide, = 0·2531 grm. mercury.

	Calculated for N_3Hg.	Found.
Hg	82·65	82·72 per cent.
N_3	17·35	17·31 ,,
	100·00	100·03 ,,

Nitrogen calomel, if covered with ammonia water, forms a black insoluble compound.

Nitrogen Lead, N_6Pb,

Is precipitated from a solution of the sodium or ammonium salt on the addition of lead acetate; the precipitate is soluble in an excess of the precipitant. It is drained and frequently washed with water.

I. 0·1157 grm. substance yields with dilute sulphuric acid 0·1209 grm. $PbSO_4$, representing 0·0826 grm lead.

II. 0·1592 grm. of the substance evaporated down with dilute sulphuric acid gave 0·1665 grm. $PbSO_4$, representing 0·1137 grm. lead.

	Calculated for PbN_6.	Found.	
		I.	II.
Pb	71·13	71·33	71·40

Nitrogen lead is insoluble in cold water, and much more sparingly soluble in boiling water than lead chloride. According to superficial experiments, boiling water dissolves about ½ grm. of the substance per litre.

ON CHEMISM IN LIVING PROTOPLASM.

By Prof. W. PREYER and G. WENDT (of Berlin).

(Continued from p. 288).

PROTOPLASM has a reticular structure. We may call it a highly complicated mixture or a kind of emulsion if we extend as far as possible the idea indicated by this word, and complete it by the determination that even in the free, non-nucleated, non-membranous protoplasm, which has not yet at any point reached a permanent differentiation, there is present a reticular or, as Bütschll names it, a comb-like (*wabige*, from wabe, a bee's comb) structure. Solid particles are suspended in the liquid, but even where every part seems physiologically equivalent to every other part, and not a trace of morphological individualisation is present, since separated portions are like whole, a mesh-work is still recognisable.

This architecture itself is mutable in one and the same object; in extended pseudopods it is indistinguishable, but visible in those half retracted, depending on the conditions of the surroundings in their often scarcely perceptible changes, as is proved by the observation (prolonged for hours) of living protozoa and the difference of the glandular cell protoplasm in action and in repose; and if the number of the chemical elements which can be isolated from any given protoplasm scarcely exceeds a dozen, the number of the combinations of these elements in such protoplasm is incalculable, because the compounds are themselves fluctuating.

The characteristic feature of protoplasm is its chemical and morphological variability, which, for every protoplasm adapted to given external conditions, still always leads us back to the same final products of metabolism. e.g., carbon dioxide, and thus, notwithstanding the otherwise unlimited impressionability, implies for these processes of metabolism something in common.

But if innumerable substances mutable in the highest degree, especially albumens—some of which have been recognised in protoplasm—have shown for thousands of years not the slightest tendency to a chemical equilibrium or to a transition to stable combinations, as long as the protoplasm is alive, and therefore bid defiance to every chemical empiricism, if amidst endless variations a substance without parallel in its capacity for reactions, and yet completely devoid of characters in the opinion of theoretical chemistry, can be preserved through generations untold, we have a full proof that something other than ordinary chemical reactions has existed in it, in the living protoplasm down to the present day, and that there exists no prospect of ever explaining its peculiarity by such considerations.

In particular, the absence of chemical equilibrium proves the absence of mass action in the specific processes in question. In the living protoplasm in the cell that action of mass disappears, which in all chemical reactions ever tends to react chemical equilibrium. If it is objected that perhaps the time is wanting which is necessary for the termination of the reactions, and consequently for the attainment of chemical equilibrium and of stable compounds, which are not merely constituents of frame work or excretory matters, as a continued flux from cell to cell sweeps the newly formed substances too rapidly onward, it is clear that from cell to cell—indeed, in reproduction from organism to organism—more time is constantly given, and that in the enormous intervals since protoplasm came into existence a chemical equilibrium must long ago have been reached. But no rest ensues, as, for instance, in the formation of rocks. On the contrary, protoplasm in the course of the development of plants and animals has become increasingly sensitive and prone to decomposition.

For the chemical lability* of the protoplasm in the brain of vertebrate animals is greater than that of the infusoria, the chemism of the former involves more special conditions than that of the latter.

We must here always keep in mind that protoplasm is, in fact, immortal. Whatever external injurious agencies may in however short a time convert however many individuals into inorganic matter, i.e., kill them, the root still remains. By the ovum, by the seminal filaments, even by the products of a sexual self-division (if such occurs without the antecedent contact of two protoplasmic structures), the physiological properties of the most ancient living being are inherited through all generations ; but there is no heredity without a material substratum. The sole substratum of hereditary properties is protoplasm, which therefore must have preserved itself for millions of generations. And that there is no prospect of its entire annihilation is proved by the strict validity of the law of the " preservation of life."

In each single generation in each single function of each individual it is, again, the variability of protoplasm, its metabolism, its assimilation and dissimilation, which ever and ever, in an endless succession, effects with the same few organic elements the most highly complicated chemical synthesis and transformations. It sounds paradoxical, but we can scarcely express it otherwise :—

What is permanent in protoplasm is its variability. Its unparalleled lability can manifestly not be rendered intelligible by the theory of substitution by chemical affinity, by the theory of the action of masses, however many well-characterised compounds may have been obtained from protoplasm, i.e., produced, doubtless, in part by the act of

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* " Lability," the antithesis to stability,—a useful term.

preparation, and though even the occasional substitution of one element for another has been effected without an interruption of vital activity.

(To be continued).

TREATMENT OF ZIRCONS IN PREPARING PURE ZIRCONIUM CHLORIDES.

By F. P. VENABLE.

LINNEMANN (*Sitz. Ber. Kais. Akad. d. Wissenschaft*, vol. ii., 1885, translated in the CHEMICAL NEWS, vol. iii., 233 and 240) has published an account of the " Treatment and Qualitative Composition of Zircon." All previous methods of breaking up the zircon and purifying the zirconia have presented numerous difficulties and proved decidedly unsatisfactory.

Having occasion to prepare some of the compounds of zirconium in considerable quantity and of chemical purity, I adopted the methods of Linnemann. In the course of my work, I have found it advisable to modify the process in several respects, and I make this publication in order that my experience may be available, and perhaps serviceable, to others.

In the first place, I have found the mechanical preparation can be simplified. I have used North Carolina zircons, and have found it sufficient to pulverise them roughly in an iron mortar and then grind in an agate mortar until the powder passed through a 100-mesh sieve. The preliminary exposure during ten days to vapour of hydrofluoric acid and the grinding until the powder passed a silk sieve seemed both unnecessary. The fine powder was repeatedly boiled with strong hydrochloric acid and washed with water. 500 grms. treated in this way lost 17 grms., the hydrochloric acid thus dissolving 3·40 per cent of the whole. The fusions were made in nickel crucibles, which are very much cheaper and less attacked than the silver recommended by Linnemann. The loss comes chiefly in the cracking of the crucibles during the cooling after fusion. The crucibles used held a charge of 100 grms. zircon, 400 grms. sodium hydroxide, and 20 grms. sodium fluoride. This is one-half the amount of sodium fluoride recommended by Linnemann, but proved sufficient.

The sodium fluoride should be dried beforehand. The sodium hydroxide is first thoroughly melted and the fluoride then added. The mass should be brought to a fairly high temperature and then the zircon powder added. A rapid evolution of gas follows the introduction of the powder. The mass should be well stirred by means of a nickel stirrer—a narrow strip of sheet nickel fastened to a glass rod answers the purpose and keeps the hands beyond the reach of hot alkali occasionally thrown out. If the bubbles threaten to rise over the edge, temporary removal of the lamp secures their subsidence. The crucible should not be allowed to cool too far, however. Much seems to depend upon carrying through the reaction rapidly at a high temperature. I have at times doubled and even tripled the length of fusion at a lower temperature without securing the thorough breaking up of the zircons obtained at a high temperature. After the first violent boiling a quieter period follows. The end of the reaction is shown by a thickening of the mass and the rising of large bubbles here and there; also sometimes by a fine spitting or spray. In several instances where weights were kept the undissolved or unattacked portion of the zircon powder amounted to less than 0·5 per cent.

The melted mass was poured out upon pieces of sheet nickel for cooling. After solidifying enough to handle with tongs, it was broken off and plunged in a beaker of cold water. Water was also put in the crucible, after it had cooled, to dissolve off the portions adhering to the sides.

The water separates the sodium silicate from sodium zirconate, leaving the latter undissolved. The separation by means of water is far from perfect, some of the zirconate going into solution, though not enough usually to make it worth while to attempt to regain it. The sodium zirconate is dissolved in dilute hydrochloric acid and evaporated several times to dryness with fresh amounts of acid in order to drive off the hydrofluoric acid. There is a good deal of silica left with the undissolved portion. This is separated after evaporation to dryness. The dried mass is leached with dilute hydrochloric acid. There is difficulty sometimes in extracting all of the zirconium chloride in this way. Of course the solution contains large quantities of salt besides other substances. Zirconium hydroxide is precipitated from these by ammonium hydroxide, and then thoroughly washed in large jars by decantation. The crude zirconium hydroxide is next dissolved in strong hot hydrochloric acid, using as small an amount as possible. This solution is evaporated to dryness, and the crude zirconium chloride obtained placed in a large funnel and washed with a mixture of strong hydrochloric acid and four parts of alcohol. This mixture is poured upon the mass in the funnel and allowed slowly to drain through. Some zirconium chloride is dissolved, but can be recovered by evaporation. The mass in the funnel is left white, and fairly pure.

To complete the purification, this mass is taken and repeatedly crystallised from boiling hydrochloric acid, until the acid gives no test for iron, which seems the most persistent among the impurities. I have commonly found it well to repeat this crystallisation more than twenty times. The pure oxychloride is obtained in well-formed crystals of glistening whiteness. This method of crystallising from hydrochloric acid used by Linnemann is the only satisfactory one for purifying the zirconium chloride. I have tried the precipitation by hydrogen dioxide as recommended by Bailey, but the consumption of pure dioxide is very large, and a heavy source of expense, and the pentoxide or mixed oxides yielded is not nearly so convenient as the chloride for further working with.

The method described above is shorter than the tedious and expensive treatment with hydrochloric acid, alcohol, and ether. Judging from an attempt at carrying it out on a small scale, the amount of ether required in purifying the product from a kilo. of zircons would be very large indeed.

The modifications in the process have throughout the aim of cheapening and shortening Linnemann's process, and were successful in both directions, at least under the conditions under which I worked.

A qualitative analysis of the different products obtained while thus decomposing the zircon was made under my directions by Mr. John M. Morehead. It differed in several noteworthy particulars from that made by Linnemann.

In the first place, the hydrochloric acid used in the preliminary treatment of the zircon powder extracted a large part of the total tin present. Linneman does not mention tin as occurring in this solution. No lithium was discovered in any of the solutions, nor any bismuth and zinc. The list of elements found by Mr. Morehead is, therefore, shorter than Linnemann's, who reports sixteen. The list found was sodium, potassium, magnesium, calcium, aluminium, iron, lead, tin, uranium, erbium, silicon, and zirconium. Undoubtedly, a large portion of these come from foreign matter mixed with the zircons and sifted into the cracks in the crystals so as not to admit of separation. A number of the rare elements were looked for without avail. No thorough spectroscopic examination was made, however.

Mr. Morehead also made several quantitative determinations of the iron, silicon, and zirconium, resulting as follows:—

Per cent Zirconium Dioxide	62·82	62·59	63·12	62·80
,, Silica	34·10	34·20	33·52	34·10
,, Ferric Oxide ..		3·29		

Or, taking the means,

$$ZrO_2 = 62·83$$
$$SiO_2 = 33·98$$
$$Fe_2O_3 = 3·29$$

————
100·10

It is not right to calculate the iron as all in the oxidised condition, as much of it comes from the iron mortar, and can be easily separated with a magnet.—*Journal of Analytical and Applied Chemistry*, v., No. 10.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.
December 3rd, 1891.

Prof. A. CRUM-BROWN, F.R.S., President, in the Chair.

71. "*Note on the Structure of Luminous Flames.*" By ARTHUR SMITHELLS, B.Sc.

The author gives a brief summary of the various views that have been held on this subject. With one or two exceptions, there has been general agreement since the time of Berzelius that an ordinary candle flame, or the flame of coal gas escaping from a circular hole, is divisible into four chief regions: (i.) the dark inner part; (ii.) the luminous part; (iii.) a small bright blue part at the base of the flame, thinning off rapidly as it extends upwards; (iv.) a dim, scarcely visible, faintly luminous mantle surrounding the whole flame.

The explanation which the author would give of these regions is as follows:—The gas or vaporised wax, on issuing from the orifice or wick, becomes mixed with air and burns. Whether or not the flame is luminous depends on the rate at which the combustible is supplied. If slowly supplied, sufficient air is admixed with the gas for non-luminous combustion. Thus a very small gas flame is non-luminous, and so also the flame of a candle, with the wick cropped close to the wax. It is conventionally said that coal gas burns with a luminous flame; it is just as true to say that it burns with a non-luminous flame. The small non-luminous flame of coal gas, or of a short wick candle, is seen to have the same structure as a Bunsen burner, viz., a bright blue inner cone, and a pale lilac cone superposed upon it. The author supposes that we have here the same chemical changes occurring as are dealt with in the previous paper, viz., that the first combustion in the inner cone is mainly to CO_2, H_2O, CO, and H_2, and the final one in the outer cone is mainly that of CO and H_2 to CO_2 and H_2O. This is made more probable by the fact that if the gas supply be increased, the luminous tip appears just at the point where it appears in the experiment with benzene, and that even after it is considerably developed the shape of the flame betrays the persistence of the inner cone. As the gas supply is further increased, the luminous area becomes increasingly great, the relics of the two original cones being very small.

The author's view is further enforced by the simple experiment of taking a flame about 5 c.m. high from a Bunsen burner with the air holes stopped, noting the blue region at the base of the flame and the dim mantle outside it and then gradually turning on the air. The gradual transition shows unmistakably that the blue part and the mantle are the "rudiments" of the two cones of a Bunsen flame.

With regard to the luminous part, everything goes to

show that it is mainly a region where hydrocarbons are decomposed by the heat of the outer parts of the flame. The precise nature of the change is being studied by the author.

The dark inner cone contains mainly unburned gas, mixed with some products of combustion from surrounding regions.

A commonly held view that the mantle of a luminous flame is due to heated air and products of combustion is inconsistent with the above explanation, and also with the fact that in recent experiments it has been found impossible to render air luminous at the highest attainable temperatures.

The view that carbon is separated in a flame owing to the preferential combination of oxygen with hydrogen, is opposed, the author thinks, to all experimental evidence, which he is of opinion goes to show that if the oxygen supply be limited carbon will burn before hydrogen.

The author would describe a luminous flame as follows :—

(i.) An outer sheath or mantle, with (ii.) an inner bright blue portion visible at the base of the flame. These two parts correspond respectively to the outer and inner flame cones of a Bunsen flame, and mark the region where the coal gas or candle gas is burning with a large quantity of air.

(iii.) The yellow luminous part marking the region where the heat of the parts (i.) and (ii.) is decomposing hydrocarbons, setting free carbon, which rapidly glows and burns.

(iv.) The dark inner region, consisting of unburned gas, mixed with products of combustion of surrounding parts.

Novelty is not claimed for this description, but the author considers that the experiments described in the preceding paper put the matter in a somewhat new light.

72. "*The Existence of Hyoscyamine in Lettuce.*" By T. S. DYMOND.

Lettuce has been used in medicine from early times as a sedative, but the active constituent has never been with certainty determined. The author's attention was drawn a few months ago to the mydriatic action of an extract of lettuce used in medicine. It had been prepared from the flowering plant of common lettuce according to the directions of the "British Pharmacopœia. An examination showed that the mydriatic action was due to an alkaloid. Commercial specimens of the extract of wild lettuce and of the variety of the edible plant known as cos lettuce, obtained from three different sources, together with a specimen of the dried flowering plant of wild lettuce, were all found to contain this alkaloid.

The alkaloid was most easily isolated by mixing the commercial extract with water acidified with acetic acid, adding alcohol till precipitation of nearly all the constituents of the extract occurred, filtering, evaporating the filtrate to a low bulk, filtering again, washing the filtrate with ether till free from fat, then rendering it alkaline, and extracting the alkaloid with ether. The impure alkaloid thus obtained was purified by conversion into the oxalate, and the precipitation of this salt by ether from its alcoholic solution. On recovering the alkaloid and crystallising it from chloroform, it was obtained in silky needles having approximately the same melting point and other properties as hyoscyamine, the poisonous mydriatic alkaloid existing in belladonna, henbane, and other plants belonging to the natural order *Solanaceæ*.

The identity of the alkaloid with hyoscyamine was confirmed by conversion into the aurichloride, which melted at 159·75, the melting point given by Ladenburg for hyoscyamine aurichloride being 159°. The determination of the gold and the alkaloid in the compound afforded results corresponding with the formula of hyoscyamine aurichloride, $C_{17}H_{23}NO_3 \cdot HAuCl_4$.

The amount of hyoscyamine in the extract of common lettuce does not exceed 0·02 per cent, while in the flowering plant itself it cannot be more than 0·001 per

cent. It appears that this is the first occasion on which hyoscyamine or any other alkaloid belonging to that mydriatic group has been found in a plant not a member of the natural order *Solanaceæ*, lettuce belonging to the natural order *Compositæ*.

DISCUSSION.

Professor DUNSTAN pointed out that it had been known from the time of the Greeks that lettuce had a soporific action, and as Ladenburg and others had shown hyoscyamine to be a soporific, it was now possible for the first time to explain an ancient Grecian practice.

73. "*Cryptopine.*" By D. RAINY BROWN and W. H. PERKIN, jun., Ph.D., F.R.S.

The authors have commenced an investigation on the rare alkaloid cryptopine, which occurs in small quantity in opium, and which was first isolated by J. and H. Smith (*Jahresbericht*, 1867, 523), and subsequently analysed by Hesse (*Annalen*, Suppl., viii., 209).

Analyses of the base and of several of its salts led Hesse to assign to cryptopine the formula $C_{21}H_{23}NO_5$. The authors have prepared and analysed several samples which had been purified by conversion into the oxalate and subsequent re-crystallisation from isobutyl alcohol. The mean result of five analyses was—

	Per cent.	Theory for $C_{21}H_{23}NO_5$. Per cent.
C	68·23	68·29
H	6 34	6·23
N	4·15	3·79

The oxalate, after repeated recrystallisation from water, was obtained in the form of beautiful glistening prisms, which, on analysis, gave the following numbers as the mean of four experiments :—

		Theory for $C_{21}H_{23}NO,C_2H_2O_4$.
C	59·82 per cent.	60·13 per cent.
H	5·55 ,,	5·44 ,,
N	3·31 ,,	3·05 ,,

These analyses confirm Hesse's results, and show that cryptopine has the formula $C_{21}H_{23}NO_5$.

On oxidation with potassium permanganate, cryptopine yields among other products a crystalline acid, $C_{10}H_{10}O_6$, m. p. 179—180°, which proves to be metahemipinic acid, $C_6H_2(CH_3O)_2(COOH)_2$ [1 : 2 : 4 : 5], the acid which Goldschmidt obtained from papaverine ; this result is interesting in view of the fact that metahemipinic acid, up to the present time, has only been obtained from papaverine.

The identity of the acid obtained from cryptopine with that from papaverine was proved by the fact that both yield an anhydride, $C_{10}H_8O_5$, m. p. 175°, and an ethylimide, $C_{12}H_{13}NO_4$, melting at 226°.

Cryptopine contains only two methoxy-groups, as shown by its behaviour when treated with hydrogen iodide, these two groups being situated in that part of the molecule which is converted into metahemipinic acid on oxidation.

74. "*The Action of Sodium on Ethereal Salts.* Part III. *Benzylic Orthotoluate.*" By W. R. HODGKINSON.

The behaviour of the different ethylic toluylates towards sodium was briefly referred to in these *Proceedings* in 1886 (p. 188).

In all cases their behaviour is different to that of the ethylic salts of phenylacetic acid. No trace of any substituted acetic or benzenoid fatty acid could be found, and the action differs moreover in that no ring condensation appears to take place, as is the case with ethylic phenylacetate, which affords "triphenylphloroglucol."

In the case of the benzylic salt of orthotoluic acid, it was thought that either the CH_2 might act in a similar manner to the CH_2 in phenylacetic acid, or that two molecules would condense, forming dimethylanthraquinone and benzylic alcohol.

Benzylic orthotoluate, $C_6H_4Me \cdot CO_2 \cdot CH_2Ph$, which

does not appear to have been previously formed, is a liquid of very pale-yellow colour which boils without the least decomposition at 315° (thermometer in vapour). Rel. den. at 17° 1·12.

As mentioned in connection with triphenylphloroglucol, the products of the action of sodium on these ethereal salts differ considerably according to the conditions of the experiment. On adding the sodium to the oil previously heated to 200° it dissolved, and the temperature rose to 250°, when an oil distilled over. This, on fractional distillation, separated into toluene and benzyl alcohol for the most part, with a smaller quantum of the original ethereal salt. The sodium salt in the retort dissolved in water, and gave on treatment in the usual manner an oil and an acid. This acid is *pure o*-toluic acid. The oil was found to consist of unchanged benzylic orthotoluate and a substance boiling at 350° (nitrogen thermometer in vapour) 360°.

This substance remained liquid at − 10° and could scarcely be a derivative of anthraquinone. Analysis shows it to have the composition $C_{22}H_{20}O_2$, which is that of a substance of the formula $C_6H_4Me.CO_2.CHPh$ (CH_2Ph).

The quantity at present disposal has allowed only of hydrolysis with potassium hydroxide, from which it appears that *only o* toluic acid is formed, and an oil which boils at about 250—280°. The matter is still under investigation.

75. "*The Gas-Volumeter and Gravivolumeter.*" By G. LUNGE.

In this note the author comments on Professor Japp's reply to his criticisms (*Ber.*, xxiv., 1656).

76. "*The Action of Sulphuric Acid on the Bromides of Hydrogen, Potassium, and Sodium.*" By F. T. ADDYMAN, B.Sc.

The author has sought to determine the extent to which hydrogen bromide is oxidised by sulphuric acid under varying conditions of mass and dilution.

He first describes experiments in which sulphuric acid ($d = 1·84$) was allowed to act on potassium bromide, from which he infers that the amount of decomposition which the hydrogen ~~bromide~~ undergoes is very nearly proportional to the ~~amou~~nt of sulphuric acid used; but it is subsequently a~~ss~~ed that the extent to which the hydrogen bromi~~de~~ and acid come into contact greatly affects the result, so that a higher percentage would be decomposed in a deep than in a shallow vessel.

In the second section of the paper, a method of preparing a solution of hydrogen bromide is described, very similar to that of Feit and Kubierschky (*C. S. Abstracts*, 1891, 1320). An account is then given of observations on the amount of change produced by sulphuric acid in solutions of hydrogen, potassium, and sodium bromides. But mere traces of bromine are liberated in solutions containing not more than about 30 per cent of sulphuric acid; and the percentage of hydrogen bromide decomposed is but small, even when as much as about 70 per cent of sulphuric acid is present.

77. "*The Iodometric Estimation of Chlorates.*" By G. McGowan, Ph.D.

Attention is called to Finkener's statement, that when Bunsen's method is applied to chlorates, less than the theoretical amount of chlorine is evolved. Experiments are then described, made in accordance with the method, and with the apparatus of which an account is given at pp. 530—536 of this year's volume of the Society's *Transactions*, which corroborate the results of de Koninck and Nihoul, and prove the accuracy of the Bunsen method; Finkener's error doubtless arose from a slight loss of chlorine. The author emphasizes the importance of carrying out all such determinations in an apparatus in which the chlorine does not come into contact with india-rubber.

NOTICES OF BOOKS.

Quantitative Chemical Analysis. Adapted for Use in the Laboratories of Colleges and Schools. By F. CLOWES, D.Sc., Professor of Chemistry in the University College, Nottingham, and J. BERNARD COLEMAN, Associate of the Royal College of Science, Dublin ; Senior Demonstrator of Chemistry in the University College, Nottingham. London : J. and A. Churchill. Small 8vo., pp. 409.

A TRULY admirable book ! Every chemist who gives it a fair examination will be convinced that it could never have been written by compilers, who too often carefully appropriate the " gangue " of the works which they prey upon, neglecting the gold. Even less could it be produced by careless, incompetent workers, heedless or ignorant of the niceties which are required for accurate work. The authors, following in this respect the sound example of Rose and Fresenius, have, as they tell us in the preface, " kept their work within moderate dimensions, firstly by omitting unnecessary theoretical matter," and secondly, by " inserting only typical, useful, and well-accredited methods."

A useful and commendable feature is the bibliography placed at the beginning of the book for the benefit of students who wish for more detailed instruction on any particular subject.

The table of contents gives in parallel columns the paragraphs and the pages where any particular subject may be found.

The first part of the book supplies general instructions, directions for weighing — carefully written — the determination of specific gravities, melting- and boiling-points, mechanical comminution, drying, solution, precipitation and general instruction in manipulation.

Part II. gives directions for simple gravimetric determination. Part III. treats of volumetry. Part IV. is devoted to general analysis, including, of course, separations. Its subdivisions are technical analysis, water analysis, and food analysis, along with which comes the quantitative examination of tannin and soaps ; and ultimate organic analysis. Part V. is taken up with gas analysis, a department which in many treatises is either very superficially treated or altogether overlooked.

An appendix supplies the preparation of gases for analytical processes, results of the analysis of typical specimens, tables of useful constants and memoranda. Lastly comes a list of the apparatus and the chemicals required for the processes prescribed in the text.

We feel it our agreeable duty to give this work our warm recommendation both for what it contains and for what it ignores.

A Graduated Course of Natural Science, Experimental and Theoretical. For Schools and Colleges. Part II. Second and Third Year's Course. For the Intermediate Classes of Colleges and Technical Schools. By B. LOEWY, F.R.A S., Examiner in Experimental Physics to the College of Preceptors, London. With sixty diagrams. London and New York : Macmillan and Co. Small 8vo., pp. 257.

THIS is a treatise on what we formerly called " natural philosophy." The author is perfectly justified in holding that such a general or introductory course should precede more special studies. We may, perhaps, take exception to the term " natural science " in the title, and submit that physical science would have been a happier expression. The words " natural " and " physical " are, of course, unmistakably synonymous, but of late years custom has more or less allotted the term " physical science " to the inorganic disciplines, physics, chemistry, astronomy, &c., confining the phrase " natural science " to biology in all its branches.

We find in this book nothing questionable or excep-

tional except it may be the contention that sound is a form of energy. On this question we feel exceedingly doubtful. It is certainly not reciprocally convertible into light or heat. Nor can we calculate its mechanical equivalent. Nor is it known to fulfil any natural function save as communicating ideas or emotions from one sentient being to another. Turning aside, however, from this doubtless unprofitable question, we may remark that this work is characterised by great clearness of exposition. The experiments are well selected and easy of performance, and the illustrations are well drawn and useful.

Elementary Inorganic Chemistry. Theoretical and Practical. With a Course of Chemical Analysis and a Series of Examples in Chemical Arithmetic. By A. HUMBOLDT SEXTON, F.R.S.E., F.I.C., F.C.S. New Edition. London: Blackie and Son, Lim. F.cap. 8vo., pp. 320.

THIS book is typically examinational. The author refers to the great number of students " presenting themselves for examination " under the Science and Art Department as his reason for keeping the requirements of the Syllabus of the Department before him in preparing his book. He, however, " has not hesitated to go beyond the Syllabus where he has felt it advisable." In his arrangement of the elements he ignores the periodic classification, and in his account of the non-metallic bodies silicon and its compounds are omitted! Among the metals, gold, platinum, nickel, cobalt, antimony, arsenic, tin, zinc, not to speak of the rarer metals, are left out.

We find a series of questions and ten pages of examination papers set by the Department.

An interesting note at the conclusion of the preface is that Part V.—the elementary course of qualitative analysis—" has been re-cast to meet the alterations in the Syllabus of the Science and Art Department." Thus we see that teachers, if they wish their pupils to " pass," have to teach, not the Science, but such portions of the Science as the Department takes for the time being into favour. The examiner in this country dictates to the teacher.

We are often encountered by the cavil that without examinations it would not be possible to separate the wheat from the chaff. We maintain that the separation takes place more easily and thoroughly in real life than at any examination. Everyone knows the splendid position which Germany takes in Science. Yet she has no works written for the use of students preparing for this or the other examination. Our system, in fact, *creates* the chaff which has to be winnowed out. We would suppress all intermediate examinations and for the final test demand the production of original work in some science. The London University now demands research, but merely in addition to, not in lieu of, " passing."

The Alkali Makers' Handbook. Tables and Analytical Methods for Manufacturers of Sulphuric Acid, Nitric Acid, Soda, Potash, and Ammonia. By GEORGE LUNGE, Ph.D., Professor of Technical Chemistry, Zurich, and FERDINAND HURTER, Ph.D., Consulting Chemist to the United Alkali Company, Limited. Second Edition, enlarged and thoroughly revised. London: Whittaker and Co., and G. Bell and Sons. Small 8vo., pp. 184.

THIS work, which belongs to the " Specialists' Series," issued by the publishers above named, must be pronounced exceedingly useful.

The first edition appeared as the Alkali Makers' Pocket Book, but an increase of size has indicated its present title. The fundamental purpose of the work, entertained by a number of German alkali makers and technical chemists, was to furnish, for each raw material, and for

each product intermediate, fixed, or secondary, some one analytical process.

This one process should in each case be the best known, understanding by " best " the most convenient and expeditious as well as the most accurate. This agreement was necessitated by the number and the magnitude of commercial transactions in connection with the alkali manufacture. Hence it was of great importance to have what we may call authorised methods by which each party to a contract or to a lawsuit should be prepared to stand or fall. These standard methods have been, we are told, accepted to a very great degree by German alkali makers, by their customers, and by commercial analysts. The work has been issued also in the English language, in the hope that its leading principle may be accepted in this country also. This seems to us a most laudable undertaking, as calculated to prevent unedifying disputes. It has been necessary to recalculate a number of tables here given in accordance with British weights and measures. Had we adopted the principle—we do not say the nomenclature—of the metric system, this labour might have been saved.

We first find here a table of the atomic and equivalent weights, symbols, and valencies of the elements, round numbers being made use of. The authors have thought fit to give tungsten the name " Wolframium," which, as they cannot help knowing, is not used in the English language. Of more importance is the fact that, following the lead of the " Potash Convention," they give for platinum the obsolete atomic weight 197·18. This is the more remarkable as Continental authorities have always taken up their parable against the British alkali trade for still giving to sodium the atomic weight 22.

Another table gives the more accurate weights of the elements according to Professor Ostwald.

The table of factors for calculating grammatical analyses is in principle like that met with in Rose's " Quantitative Analysis," and will be valuable and trustworthy except where the erroneous atomic weight of platinum interferes.

After a number of other tables important to alkali manufacturers, chemists, and managers, we come to the special part including the analytical process recommended. Due attention is here paid to gas analysis, without which it is no longer practicable to conduct alkali works safely and successfully. It is remarkable that whilst the quantity of sulphurous acid escaping into the atmosphere from any other source is now strictly defined, that generated by the consumption of coal or coke is placed under no restrictions. What penalties would be incurred by any chemical manufacturer who should keep up in or around his works an atmosphere like that found in certain parts of the Underground Railway?

We feel certain that this " Handbook " will find numerous and appreciative readers among all persons connected with the alkali trade.

A Handbook of Industrial Organic Chemistry, adapted for the use of Manufacturers, Chemists, and all interested in the Utilisation of Organic Materials in the Industrial Arts. By S. P. SADTLER, Ph.D., F.C.S. London and Berlin, Member of the Society of Chemical Industry, &c. Philadelphia: J. B. Lippincott and Co. 8vo., pp. 519.

THE author of this treatise states that in the English language we have in general chemical technology " only the now antiquated technology of Wagner and Payen." He qualifies this assertion, however, by admitting that he refers " only to general works on chemical technology of moderate size." Dr. Sadtler must be aware that to compress a general view of chemical technology within a single volume of moderate size is becoming more and more difficult, if the accounts of the various processes are to enter sufficiently into useful details. In works dealing with single departments of the chemical arts our litera-

ture is fairly rich. To many of these works, indeed, he refers in the bibliographical notes placed at the end of each subject. Of course the author economises space by confining himself in this work to the organic chemical industries. This distinction, however, is difficult to carry out. Thus we find here included the manufacture of inorganic mordants, brief sections on the purification of water for industrial uses, an account of dynamite and some of its kindred bodies, &c. On the other hand, matches, phosphorus, and chemical manures are omitted, though a large portion of their ingredients must be pronounced organic. The oxalic, tartaric, citric, and malic acids do not seem to have fallen within the author's plan, no more than quinine, morphine, &c. We might naturally have expected that of quinine, which is now obtained on so extensive a scale. These omissions are the more remarkable as the author describes himself as chemical editor of the United States Dispensatory, Professor of Chemistry in the Philadelphia College of Pharmacy.

The bibliographical sections we have already pronounced useful, but their value would have been increased if the name of the publisher of each work had been given. To say that a book is published in London, Paris, or Leipzig, as the case may be, is often insufficient.

As regards the subject matter of the work, its general character is correctness. Still greater details would in many cases have been highly desirable. In some cases the arrangement adopted is, at least, peculiar. Thus we find nitroglycerin and dynamite under the head " Fats and Fatty Oils," whilst their near neighbour gun-cotton is to be sought under " Vegetable Textile Fibres." Printing inks come under " Essential Oils and Resins," and writing inks apparently nowhere.

Great care has evidently been expended on getting up the statistical appendices.

A Practical Introduction to the Elements of Chemistry.
By W. MARSHALL WATTS, D.Sc. (Lond.), B.Sc. (Vict.), F.I.C. London: Nisbet and Co. Small 8vo., pp. 128.

THIS little work belongs to a series entitled " Nisbet's Elementary Science Manuals," prepared, it is stated, for the " Oxford and Cambridge Local Examinations," though they are also intended for " School and Family Use."

In the preface, the author, or else the general editor, Rev. J. H. Whitehead, M.A., whose functions do not very clearly appear, informs us that the " plan of the present work differs somewhat from that usual in small books of a similar title." It is " experimental from the very beginning." So numerous, however, are the elementary manuals of chemistry used, or at least published, in this country, and so slight are the shades of difference between them, that we cannot venture to say in how far the author's claim can be substantiated. Our own opinion is that there is here little, if anything, which has not already been said clearly and repeatedly.

CORRESPONDENCE.

NEW METHYLATED SPIRIT.

To the Editor of the Chemical News.

SIR, – I have read the note on "new methylated spirit" in the CHEMICAL NEWS (vol. lxiv., p. 310), and at the council meeting of the Royal Microscopical Society on Wednesday last I had some conversation on the subject of the new regulations and gave notice of my intention to bring it before the next meeting.

By the new order histologists are deprived of their most valuable reagent. Alcohol in histology, like sulphuric acid

in chemistry, is the key to most of the work, and a heavy duty on either would bring work to a standstill.

Among the societies whose members are affected besides the Royal Microscopical, are the Chemical, Photographic, Linnean, Zoological, &c. Hospitals, large museums, and medical schools are able to obtain quantities of 5 gallons and upwards of the old kind of spirit ; but small laboratories and the whole race of amateurs must either leave off work or pay the duty of ten shillings and sixpence per gallon. Truly " endowment of research " with a vengeance !

We considered at the Royal Microscopical Society that several of the other societies might take united action in the matter, and bring a little pressure to bear upon the Inland Revenue authorities, who, we may charitably suppose, are quite ignorant of the mischief they are doing.

I should be glad if you could in any way aid me in this matter.—I am, &c.,

W. T. SUFFOLK.

December 19th, 1891.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances, de l' Académie des Sciences. Vol. cxiii., No. 23, December 7.

Reply to a Paper by M. Besson on Boron Phosphide.—Henri Moissan.—A question of priority.

The Works of Scheele.—M. Nordenskiold, in a letter addressed to M. Berthelot, announces that he has undertaken the publication of the hitherto unpublished letters and memoirs of Scheele. The letters are composed in a clear and concise style. They contain exclusively accounts of chemical experiments, novel, and generally important. There scarcely ever occurs in them a useless phrase which might be suppressed or modified.

Report on the De-plastering of Wines.—The Syndical Chamber of the wine and spirit trade of Paris and the Seine apply for the opinion of the Academy on the use of the salts of strontium for de-plastering wines.

Vapour Tensions of Solutions of Cobalt Chloride.—Georges Charpy.—Referring to Etard's recent paper on the solubility of cobalt chloride, the author has observed facts of the same order whilst studying the vapour tensions of the solutions of cobalt chloride. The facts, like those observed by Etard, lead us to admit the existence of two stable conditions of cobalt chloride. This change of condition may be ascribed either to a variation in the state of hydration of the salt, or to a change in its molecular aggregation.

Action of Sodammonium and Potassammonium upon Certain Metals.—M. Joannis.—Sodammonium and potassammonium are decomposed by several metals, especially by mercury, lead, and antimony. Sodammonium is without action upon aluminium, silver, lead, and copper. The author examines in detail the action of these two compounds upon mercury and lead. With an excess of lead he obtains a compound, $Pb_4Na,2NH_3$, of deep indigo blue colour, which dissolves in ammonia with a bottle-green colour.

Calculation of the Temperature of Ebullition of the Isomeric Ethers of the Fatty Acids.—G. Hinrichs.—This paper cannot be reproduced without the accompanying diagram.

Thermic Data on Active Malic Acid and the Potassium and Sodium Malates.—G. Massol.—This paper does not admit of useful abridgment.

The Rotatory Power of Silk.—Leo Vignon.—Silk ranks, as regards its chemical constitution, among the albumenoid substances. If treated in heat with dilute sulphuric acid it yields among its decomposition products leucine and tyrosine. The solutions of the two principal portions of the silk of *Bombyx mori* (the " gum " in soda and the fibroine in hydrochloric acid) both exert a considerable action upon polarised light. Both are strongly lævo-rotatory, their rotatory power being close upon $-40°$.

Ammonia in Atmospheric Waters.—Albert Lévy.— The author questions the values given by MM. Marcano and Muntz in their recent memoir. He notes that in England Messrs. Lawes and Gilbert obtained in 1856 1·43 m.grm.—a figure very close upon that obtained in Caracas. His own analyses of the rains falling at Montsouris during the last sixteen years (a yearly mean of 150 showers), give an average weight of 2·2 m.grms. of ammonia per litre of water, a figure higher than that obtained at Caracas.

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Zeitschrift fur Analytische Chemie.
Vol. xxx., Part 4.

Studies on the Ripening of Cherries, on the Fermentation Products of Cherry and Currant Juice, and on the Colouring-Matter of the Red and the Black Currant.—W. Klein.—This memoir, which runs to 25 pp., and includes seven tables and a plate showing the absorption-spectra of the products, does not admit either of useful abstraction or insertion in full.

Antimony Pentasulphide.—Th. Wilm.—According to the author the compound met with in commerce as " golden sulphuret " is not always an antimony penta-sulphide (Sb_2S_5), but a mixture of antimony tersulphide with free sulphur, or of the penta- and tersulphides with sulphur. He shows that the determination of the sulphur capable of extraction by means of carbon disulphide does not lead to satisfactory results. For the determination of total sulphur he recommends oxidation with fuming nitric acid in a sealed tube. A determination in an Erlenmeyer flask did not give constant results. He heats for 2—3 hours not above 130°, when no explosion takes place. On opening the tube a little water is added, when the contents turn green or bluish-green, and a quantity of gas escapes. When this reaction is over, the glass is nearly filled with concentrated hydrochloric acid, and heated in the water-bath until the white powder is completely dissolved. The whole is then rinsed into a porcelain capsule, evaporated down as far as practicable on the water-bath, covers the moist residue with a little concentrated hydrochloric acid, applies heat and adds a solution of tartaric acid. The boiling solution is precipitated with barium chloride, and the barium sulphate filtered off after standing for 10—12 hours.

Universal Gas-Holder.—Dr. Eichhorn.—This apparatus, the construction of which cannot be described intelligibly without the accompanying figure, serves at once as a gas-holder, a blast, a compression-pump, and a rarefying apparatus.

Glass Vessels for Scientific Purposes.—Leybolds (*Cologne*).—These vessels, some of which are here figured, are cells with flat sides made of uniform thickness and free from bubbles or waviness. They are recommended for various chemical, physical, bacteriological, &c., uses.

Separation of Barium and Calcium.—R. Fresenius. —The concluding portion of a memoir which will be presently reproduced.

The Question of Introducing the True Litre, or retaining that of Mohr in Volumetric Analysis.—W. Fresenius.—The author decides in favour of retaining the litre of Mohr, *i.e.*, the volume of a kilo. of water at 175°, as weighed in the air with brass weights.

Spectra of the Elements of Mendeleeff's Second Group.—H. Kayser and C. Runge (*Annalen der Physik*). —No details are given.

Colorimetric Apparatus and Methods, and Quantitative Spectrum Analysis.—G. Krüss and H. Kruss.— A work published by L. Voss, Hamburg. No particulars are here given.

A Spectro-Colorimeter.—D'Arsonval (*Seances Soc. Franc. de Phys.*).—Already inserted.

A Graphic Table for finding the Correction of the Readings of the Barometer.—(Necessary on account of the reduction to o° for the expansion of the mercury).—R. Mehmke (*Annalen der Physik*.).—No particulars are here given.

Influence of Pressure upon the Electroconductivity of Liquids.—C. Barus (*Silliman's Journal*).—No particulars.

Distinctions between α- and β-Naphthol.—N. Yvon. —To 10 c.c. of a saturated aqueous solution of naphthol there are added: (1) Alcohol 2 c.c., nitric acid 2 c.c., mercury nitrates 10 drops; (2) alcohol 2 c.c., potassium nitrate (saturated solution) 3 drops, sulphuric acid 10 drops. These reagents produce colour reactions as follows. In α-naphthol:—Reagent 1, the yellow colour of the mixture is not changed on boiling; chloroform is coloured yellow and ether yellowish-green; gun-cotton is dyed yellow, sulphurous acid renders the mixture immediately turbid with separation of a red precipitate. Reagent 2, on the other hand, turns the reddish-brown colour of the mixture to a brown on boiling; chloroform is coloured greenish-brown, and ether a yellowish-green; gun-cotton is dyed a dirty yellow. Sulphurous acid turns the mixture a dirty green without precipitation. With β-naphthol and No. 1 reagent the intense orange yellow colour passes at once into an orange red and is not altered by boiling; gun-cotton is dyed a rose red; the mixture colours chloroform a ruby red, and ether a yellow. Sulphurous acid gives the mixture a rose colour, which disappears very gradually, whilst a yellow or black precipitate is formed. With reagent No. 2 there is produced an intense violet red not changed by boiling; gun-cotton is dyed a vinous red, chloroform is coloured a greenish yellow and ether a yellow; the red colour is at once destroyed by sulphurous acid, but without precipitation. By means of these reactions the author succeeded in detecting β-naphthol in urine, but not α naphthol.

Detection of the Amines of the Aromatic Series.— Ch. Lauth (*Comptes Rendus*).—Already inserted.

Elementary Analysis of Volatile Liquids. — E. Reichardt (*Archiv. der Pharm*).—Very volatile liquids are weighed off in a small glass tube which fits into the platinum boat to be used. The glass tube is sealed below, rounded off above, and may be closed with a cork. It is half filled with copper oxide previously ignited, and fixed in a suitable vessel in a perpendicular position for weighing. The liquid to be analysed is now added, the tube is weighed again and filled up with copper oxide. When closed by means of a cork the liquid may thus be preserved. When the combustion is undertaken the open tube is placed in the platinum boat, the bottom of which is covered with a little copper oxide to prevent adhesion. The boat is pushed into the combustion-tube, and the combustion is then carried out in the usual manner in a current of oxygen. It is indifferent whether the open end of the little glass tube is turned towards the absorption apparatus or the closed end of the combustion tube. Experiments with volatile oils and with ethylic alcohol gave satisfactory results. In the elementary analysis of sparingly volatile liquids, we may, according to the author, place the liquid in question, drop by drop, upon the bottom of the platinum boat, previously ignited, and covered with copper oxide, and push it rapidly into the combustion-tube. An attraction of moisture is not to be apprehended.

Electro-conductivity of Boric Acid in presence of Mannite, Dulcite, and Polyvalent Alcohols.—G. Magnanini (*Rendicont della R. Acc. dei Lincei*).—The molecular conductivity of boric acid, which is *per se* smaller than 6 units, rises in presence of mannite to 300, 500, and upwards, according to the quantity of mannite. The molecular conductivity of boric acid in presence of mannite decreases with dilution.

Ascent of Solutions in Capillary Tubes, and the Law of these Phenomena.—M. Goldstein (*Zeit. Phys. Chemie*).—The author proposes the law—

$$\frac{H - h}{H.M} \; i = C,$$

where H is the height of ascent of the water, h that of the solution, M the molecular weight of the dissolved substance, i the Van 't Hoff co-efficient, and C a constant which varies with the percentage of the dissolved substance.

The Use of the Pendulum as a Balance.—K. Fuchs (*Zeit. Phys. Chemie*).—Already inserted.

Determination of Specific Gravities.—L. Amat.—From the *Bulletin de la Soc. Chimique de Paris*.

Reading Hydrometers.—C. Margoni and Grattorola (*Rendi. Acc. dei Lincei*).—In case of opaque liquids the authors apply a ring of platinum wire to the sides of the vessel in which the stem of the hydrometer goes up and down.

Apparatus for Determining the Specific Gravity of Solids.—W. Brown.—From *Industries* and *Chemiker Zeitung*.

A Thermo-Electric Battery.—Gülcher (*Elektrotech. Anzeiger*).—The elements are hollow bodies or combinations of such with massive rods. A battery of fifty elements is about equal to two Bunsen elements. The hourly working cost is 3—3½ pfennige.

Analysis of Sodium Aluminate.—G. Lunge (*Zeit. Angew. Chemie*).—Already inserted.

Separation and Determination of Antimony.—J. Thiee (*Liebig's Annalen*).—This paper will be inserted *in extenso.*

Separation and Determination of Tellurium.—E· Donath (*Zeit. Angew. Chemie*).—Already inserted.

New Method for Examining Ferrocyanides for Determining the Contents of Prussiate Melts, and of the Ferrocyanides in Spent Masses from Gas-Purifiers.—R. Zaloziecki (*Zeit. Angew. Chemie.*—Already inserted.

MISCELLANEOUS.

The Late Prof. Stas.—It is generally known that the papers of Stas are characterised not by their bulk and number, but by their sterling value. As far back as 1838 he published his researches on phloridzine. In 1849 there appeared his memoir on the true atomic weight of carbon. Two years later he communicated a valuable method for detecting alkaloids in poisoning cases. It will be remembered that he was the trusted and trustworthy adviser of the Belgian authorities on all questions of a chemical nature. In 1860 he began the publication of his *magnum opus,*—the inquiry into the reciprocal relations of the atomic weights. This long and laborious inquiry was undertaken with a view of deciding on the validity of Prout's law. As we need scarcely remind the reader, the conclusion was negative. The atomic weights examined were not found to be exact multiples by whole numbers, either of 1,—the atomic weight of hydrogen,—or of 0·5 or 0·25. On this point there arose some controversy with Prof. Marignac. But whatever may be the meaning of the remarkable fact

that the atomic weights of many elements approximate very closely to the values which Prout's law would require, the determinations of Stas have not been successfully challenged either in principle or in detail. His memoirs will be found in the earlier numbers of the CHEMICAL NEWS.

Diaries for 1892. — Messrs. Cassell and Co., the publishers of Letts's Diaries, have as usual sent us a selection for the approaching year. These are too well known and have secured too firm a hold upon the public for any detailed description to be necessary. The most generally useful to men of business will be the Rough and Commercial series, foolscap size, with a week to an opening. Those who require a smaller sized diary for the office table cannot do better than choose the Office edition, post octavo size. This contains a day on a page, and in addition gives information on postal, commercial, legal, and diplomatic matters, which are often required. However, in the list of ambassadors abroad we notice that our representative in France is still given as the Right Honourable the Earl of Lytton, whilst Mr. W. H. Smith is mentioned as the First Lord of the Treasury, and Mr. Balfour the Chief Secretary for Ireland. The Pocket editions with a week on a page are similar to the above, but smaller. The diary of most use to medical men will perhaps be the Medical Diary, which contains notes, information, and headings specially required in practice. It would be of great value to all our readers if Messrs. Cassell could see their way to bring out a similar diary for the use of men of science and chemists in general. Besides these there are a series of pocket books for ladies and gentlemen, which contain memoranda likely to be of special interest.

MEETINGS FOR THE WEEK.

TUESDAY, 29th —Royal Institution, 3. "Life in Motion, or the Animal Machine," by Professor John G. McKendrick.

THURSDAY, 31st.—Royal Institution, 3. "Life in Motion, or the Animal Machine," by Professor John G. McKendrick.

SATURDAY, Jan. 2nd.—Royal Institution, 3. "Life in Motion, or the Animal Machine," by Professor John G. McKendrick.

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